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Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

ENGLISH TRANSLATION OF A SERIES OF TWELVE JAPANESE PAPERS ON ANODE PASSIVATION IN COPPER REFINING

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Impurities in Copper Refining

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ENGLISH TRANSLATION OF A SERIES OF TWELVE JAPANESE PAPERS ON ANODE PASSIVATION IN COPPER REFINING

by

J.E. Dutrizac*

ABSTRACT

As part of CANMET's new Impurities in Copper Refining project, a series of twelve Japanese papers by Abe and Goto was translated into English by the Translation Bureau of the Multilingual Services Division of the Secretary of State. These papers represent a systematic study of the effect of oxygen, impurities, electrolyte composition and operating conditions on the passivation of copper anodes under commercially meaningful conditions. Useful data on the slimes layer formed during electrolysis are also presented. In general, any condition which causes a solid layer to form on the corroding copper anode increases the likelihood of passivation.

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TRADUCTION ANGLAISE D'UNE SÉRIE DE DOUZE ÉTUDES ÉCRITES EN JAPONAIS AU SUJET DE LA PASSIVATION ANODIQUE LORS DE L'AFFINAGE DU CUIVRE

par

J.E. Dutrizac*

RÉSUMÉ

Dans le cadre du nouveau projet de recherche de CANMET sur les impuretés dans l'affinage du cuivre, une série de douze études écrites en japonais par Abe et Goto ont été traduites au Bureau de traduction de la Direction des services multilingues du Secrétariat d'État. Ces études décrivent l'étude systématique de l'effet de l'oxygène, des impuretés, de la composition électrolyte et des condition de marche sur la passivation des anodes de cuivre dans des conditions significatives commercialement. Des données utiles sur les couches de boues dont la formation a eu lieu durant l'électrolise sont aussi présentées. En général, toute condition causant la formation d'une couche solide sur l'anode de cuivre corrodante, augmente les chances de passivation.

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INTRODUCTION

CANMET, in close co-operation with the Canadian copper industry and the academic community, recently inaugurated a project on Impurities in Copper Refining. The objectives of the project include the prevention of anode passivation, copper cathode quality and anode slimes processing to recover valuable elements like gold, silver and selenium. Anode passivation appears to be a significant industrial problem as it results in increased energy consumption and decreased refinery utilization.

Recently, a series of twelve Japanese papers by S. Abe and S. Goto appeared in the open literature. The published abstracts of these papers outlined a comprehensive study of many key areas of the anode passivation problem including the effects of oxygen, impurities, electrolyte composition and operating conditions. Novel experimental methods were suggested and new information on the composition and structure of the anode slimes was presented. There was a strong feeling in both CANMET and the industry that all the information contained in the twelve Japanese papers should be made readily available. Accordingly, the Translation Bureau of the Multilingual Services Division of the Secretary of State was approached, and "unedited" English translations of the twelve Japanese papers were produced for the information of the project participants. The technical terminology was verified and certain major grammatical errors in the translations were corrected at CANMET prior to the incorporation of the translations into this report.

RESULTS

Table 1 lists the titles, authors and references of the twelve translated papers presented in this report. Additional information on the Japanese titles, etc. is contained on the Library Identification form which preceeds each translated article presented.

Table 1 - A listing of the titles, authors and references of the twelve Japanese papers translated for this report; the Page No. refers to the pagination in the current report.

Page No.	English Title	Authors	Japanese Reference
5	A mechanism of the cathodic reduction of Cu_2O phase present on the surface of a copper anode - Anode passivation in copper refining (1st Report)	S. Abe, S. Goto and N. Masuko	Nippon Kogyo Kaishi 97(1120), 479-482 (1981)
18	The origin of Cu_2O phase present in a layer of anode slimes - Anode passivation in copper refining (2nd Report)	S. Abe and S. Goto	Nippon Kogyo Kaishi 97(1121), 549-553 (1981)
34	A mechanism of $CuSO_4$ salt formation on the surface of passivating copper anode - Anode passivation in copper refining (3rd Report)	S. Abe and S. Goto	Nippon Kogyo Kaishi 97(1123), 951-956 (1981)
54	A mechanism of the copper powder formation on the surface of an anodizing copper anode - Anode passivation in copper refining (4th Report)	S. Abe and S. Goto	Nippon Kogyo Kaishi 97(1125), 1193-1198 (1981)
75	Effect of anode oxygen upon passivity of copper anodes - Anode passivation in copper refining (5th Report)	S. Abe and S. Goto	Nippon Kogyo Kaishi 97(1126), 1289-1294 (1981)
97	Effect of sulfuric acid concentration in copper electrolyte upon the passivity of copper anodes - Anode passivation in copper refining (6th Report)	S. Abe and S. Goto	Nippon Kogyo Kaishi 98(1127), 41-45 (1982)

Page No.	English Title	Authors	Japanese Reference
112	Effect of electrolyte temperature upon passivity of copper anodes - Anode passivation in copper refining (7th Report)	S. Abe and S. Goto	Nippon Kogyo Kaishi 98(1128), 113-117 (1982)
134	Effect of anode oxygen level upon the dissolution characteristics of copper anode - Anode passivation in copper refining (8th Report)	S. Abe and S. Goto	Nippon Kogyo Kaishi 100(1151), 53-58 (1984)
155	A phase conversion $Cu_2O \rightarrow CuO + Cu^o$ occurring in the matrix of copper anodes during the annealing/ slow cooling process - Anode passivation in copper refining (9th Report)	S. Abe and S. Goto	Nippon Kogyo Kaishi 100(1152), 97-101 (1984)
169	Dissolution characteristics of thermally activated copper anodes - Anode passivation in copper refining (10th Report)	S. Abe and S. Goto	Nippon Kogyo Kaishi 100(1153), 253-258 (1984)
193	Effect of anode impurities upon passivity of copper anodes - Anode passivation in copper refining (11th Report)	S. Abe and S. Goto	Nippon Kogyo Kaishi 100(1155), 429-433 (1984)
207	Some considerations on the structure of an anode slime layer - Anode passivation in copper refining (12th Report)	S. Abe	Nippon Kogyo Kaishi 100(1156), 519-522 (1984)

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Japanese	English

Author - Auteur

Shinichiro ABE, Sakichi GOTO and Noboru MASUKO

Title in English or French - Titre anglais ou français

A Mechanism of the Cathodic Reduction of Cu_2O Phase Present on the Surface of a Copper Anode. -Anode Passivation in Copper Refining (1st Report)-

Title in foreign language (Transliterate foreign characters)
Titre en langue étrangère (Transcrire en caractères romains)

Ryusando Yoekichu deno Cu_2O so no Inkyokukangenkiko --Doyokyoku Fukotaika no Kenkyu (Dai Ippo)--

Reference in foreign language (Name of book or publication) in full, transliterate foreign characters.
Référence en langue étrangère (Nom du livre ou publication), au complet, transcrire en caractères romains.

Nihon Kogyo Kaishi

Reference in English or French - Référence en anglais ou français

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A Mechanism of the Cathodic Reduction of a Cu_2O Phase Present On the Surface of a Copper Anode*

- Anode passivation in copper refining (1st Report) -

by Shinichiro ABE[1], Sakichi GOTO[2] and Noboru MASUKO[3]

A simple electrochemical method has been established to detect a Cu_2O phase present or newly formed on the surface of a copper anode. Utilizing this technique, a study has been extended to investigate conditions which allow this oxide phase to form during anodization.

A well-defined peak corresponding to the reduction of a Cu_2O phase appears on the cathodic voltammetric curve provided a sufficiently fast potential-sweep rate is employed (i.e., >0.6 V/min). This reduction reaction proceeds through the following three sequential steps:

$Cu_2O + 2e^- \rightarrow 2Cu^o + O^{2-}$ (electron transfer)

$Cu^{2+} + O^{2-} \rightarrow CuO$ (rate-determining)

$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$ (following reaction)

The overall cathodic reaction is expressed by:

$$Cu_2O + Cu^{2+} + 2e^- \rightarrow 2Cu^o + CuO$$

and its equilibrium potential as calculated from the Nernst's equation based on the present experimental conditions is -0.42 V vs Hg/Hg_2SO_4, which coincides very well with the experimental value.

Various anodizing conditions were given to a pure Cu anode, and analysis of the results indicates that a Cu_2O phase only forms when the copper anode is passive.

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* Received April 14, 1980.

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a) Identified as $CuSO_4.5H_2O$ as a result of XRD analysis.

1. Introduction

When copper and copper alloys undergo anodization in a pH range greater than weakly acidic, polarization curves of the so-called "pseudo-passivation" type are obtained, and this phenomenon is caused by a porous Cu_2O film formed on the surface of the anode.[1)]

On the other hand, when a copper anode undergoes anodic polarization in a strongly acidic copper electrolyte, the passivation observed is essentially caused by the production of a non-conductive copper sulfate[a)] film which is deposited on and attached to the electrode.[2)] It is said that a Cu_2O phase is produced simultaneously, and it is also said that under such strongly acidic conditions it is unlikely to be formed. It is however a fact that these copper oxides are detected as the main component in natural slime.[2)]

When crude copper containing a fair amount of Cu_2O phase or even a pure copper electrode

which has been made forcibly passive are polarized toward the cathode with an appropriate potential sweep rate, a sharp reduction wave is observed to appear at about -0.42V before the appearance of the potential corresponding to copper ion reduction deposition (peak potential : -0.55V vs. Hg/Hg_2SO_4, the same hereafter). Based on the electrode/solution system used in this study, this reduction wave corresponds very likely to the reduction reaction of the Cu_2O phase.

Thus, we report here the results of studies on identifying the reduction wave, and based on the electrochemical findings thus obtained, the mechanism of the formation of the Cu_2O phase in pure copper anodes is discussed. The research results on the formation of the Cu_2O in the slime produced during electrolytic purification of actual crude copper will be reported later.

2. Experimental Method

Electrical copper and crude copper prepared by INCO Metal Company Limited were the 2 types of copper anodes used. With regard to the latter type, an on-site crude copper piece was redissolved in the laboratory and the oxygen content was adjusted from 210 ppm to 7200 ppm by graphite reduction or by adding powdered reagent-grade Cu_2O. Table I shows the sample numbers and the oxygen contents.

With the oxygen content adjusted, the cooled mass was used for cutting out small cubes which were pressed into acrylic resin, and electrodes with exposed areas of 1.69 cm^2 (crude copper) and 2.25 cm^2 (pure copper) were prepared for the experiments.

From the results of preliminary experiments it was found that the electrodes with polished surfaces showed clearer reduction waves of the Cu_2O phase, and thus, a mirror surfaced electrode was used as a basic rule for the cathodic polarization measurements by the potential sweeping method.

The test solution was a synthetic copper refining solution with a composition (in g/L) of 40 Cu, 20 Ni and 200 H_2SO_4, with no organic additives. The measurements were taken without stirring at 50°C, and with potential sweep rates of 0.6 to 6V/min.

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3. Experimental Results

(1) Anodic Reduction Mechanism of the Cu_2O

When the potential was run in the cathode direction at rates greater than 0.6 V/min on the pure copper and on the high oxygen crude copper (G7, 7200 ppm), the reduction curves shown schematically in Figure 1 are obtained. The reduction waves at -0.55 V, which are common to both cases, are considered p.480 to correspond to copper ion precipitation, but the other reduction wave at approximately -0.42 V has the characteristic that this can only be obtained with copper samples that contain sufficient oxygen. Then the results of preliminary experiments showed that this reduction wave is very sensitive to changes in oxygen content in the coudse copper samples, and also showed that enough copper ions and free sulfuric acid must be simultaneously present in the copper test solution.

For these 2 types of reduction waves which appear on the cathodic polarization curves of pure and crude copper G7, Table 2 shows the analytical results of how the potential sweep rates affect the nature of the peak potentials and the peak currents. First, when the reduction wave at -0.55 V is considered, if the sweep rate is increased 10 times, the peak potential moves 15 mV in the base direction, and so from the relationship[3] $\Delta E=30/n$ (mV), this is considered to be a 2 electron reduction reaction ($Cu^{2+} + 2e^- \longrightarrow Cu^0$). On the other hand, because the reduction wave at -0.42 V moves in the base direction 31 mV for the same increase in sweep

rate, it corresponds to a one electron reaction. Also, if both reduction reactions —regardless of reversibility or not — do not have any other following reactions, a plot of $ip/V^{\frac{1}{2}}$ vs. $V^{\frac{1}{2}}$ should give a horizontal linear line.[3] This relationship is plotted here in Figure 2, and the horizontal relationship can be clearly seen for ip(1) and ip(2).[b] However, because such a horizontal line cannot be obtained for the ip(3) case, this suggests that in this reduction reaction there appears some other reaction following the one electron reduction reaction. In addition, as described earlier, this reduction wave appears only when there is sufficient free sulfuric acid present, and also, the peak current density increases in direct proportion to the copper ion concentration (Figure 3). That is, it can be considered to be controlled by the dispersion of the copper ions to the anode side.

When all of these facts are considered, the reduction wave at -0.42 V appears to proceed through the following three elementary processes.

$Cu_2O + 2e^- \longrightarrow 2Cu^o + O^{2-}$ .....(1): charge transfer step

$Cu^{2+} + O^{2-} \longrightarrow CuO$ .....(2): rate-determining step

$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$.....(3): other secondary reaction

Now, combining (1) and (2) gives the following:

$$Cu_2O + Cu^{2+} + 2e^- \longrightarrow 2Cu^o + CuO \quad \text{.....(4)}$$

and when the Nernst equilibrium potential is obtained using these experimental conditions,[c] one finds :

$$E = 0.237 + (0.064/2)\log a_{Cu^{2+}} \quad \text{.....(5)}$$

$$= -0.42 \text{ V} \quad \text{vs.} \quad Hg/Hg_2SO_4$$

and this shows good agreement with the experimental results.

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b) In the case ip(2), because the crude copper electrode surface contains impurities, the linearity appears to be not as good.

c) The average activity coefficient at 50°C and 40 g/l Cu^{2+} was taken to be 0.5.

In order to add further support to the reduction mechanism (4), the following analysis was carried out. The changes in the peak potentials which give ip(3) were obtained by changing the test solution copper ion concentrations (0 ~ 75 g/l), and the results are shown in Figure 4; the slope of the line thus obtained is about -32 mV/div, which corresponds to n = 2 in the equilibrium potential equation (5). This indicates that 2 electrons are involved in equation (4). That is, in the compound Cu_2O there are 2 moles of Cu, and it is essentially the same as the involvement of one electron. Also, in order for reaction (4) to proceed rapidly to the right, the CuO, which is the intermediate substance produced by the rate determining step (2), must be removed from the electrode system. This aspect is the reason why the presence of a sufficient amount of free sulfuric acid is required in order to give a clear reduction wave. p.481

As another test, combining equations (1), (2) and (3) gives the following equation:

$$Cu_2O + 2H^+ + 2e^- \longrightarrow 2Cu^o + H_2O \quad \text{.....(6)}$$

and then if the equilibrium potential is calculated, the value obtained is E = -0.17 V, which is quite different from the experimental value. This equation is defective because it does not express the so-called "catalytic action" of the copper ion as reflected in equation (4).

From the above discussion it can be concluded that the reduction wave at -0.42 V corresponds to the reduction of the Cu_2O phase present in the coarse copper. Experimental results which seem to further support this conclusion are shown in Figure 5. Here the changes in ip^{Cu_2O} values for INCO crude copper with varying amounts of oxygen are plotted versus the oxygen levels. It is clear from this Figure that above a certain concentration of oxygen (about 850 ppm)

density almost
the reduction current increases linearly with the oxygen content.

(2) Conditions for Cu_2O Generation on a Pure Copper Anode

A pure copper electrode was anodized in a standard copper solution using a potential sweep rate of 0.06 V/min. Then, to obtain the results shown in Figure 6, the sweep was stopped when the electrolyte current reached the potentials as given for $i_k(1)$ (0, no polarization), $i_k(2)$, $i_k(3)$ (both in the active electrolytic region) and then $i_k(4)$ (Flade potential); the sweep rate was then reset at 1 V/min and immediately thereafter, sweeping was performed in the cathode direction to observe whether there was an appearance of the Cu_2O reduction wave in the vicinity of -0.42 V. Also, for the anodic currents (5) and (6), the pure copper anode was directly set at potentials of -0.1 V and 0 V, and then after the anodic current decreased to near the value shown in Figure 6, a similar cathodic sweep was immediately carried out.

The fact which became clear from this experiment is that there is no evidence of the formation of a Cu_2O phase on the electrode as long as pure copper is actively undergoing electrolysis. Only when the set potential is brought to the Flade potential does the reduction wave begin to appear. Further, when the set potential is made more noble and anodization occurs in the passive region, the Cu_2O reduction wave clearly shows up. In this Figure the peak potential of the reduction wave does not appear at -0.42 V, but in the vicinity of 0.40V which is more noble and this appears to be caused by the fact that as a result of anodization, the copper ion concentration increased near the electrode, and the cathode polarization measurement was taken (Figure 3) before the equilibrium concentration (40g/l.) was reestablished.

As has been described above, in order to generate the Cu_2O phase on a pure copper anode, it is essential that the polarization be brought up to the Flade potential.

Next, an experiment was carried out to confirm the above conclusion. Here, the pure copper anode was anodized in the standard composition electrolyte (described above) at 50°C and 200 A/m^2 for various time periods ranging from 0 to 60 minutes, and then after producing the slime (that is, fine copper powder), immediately the potential was swept to the cathode in the same experimental solution. Figure 7 shows the results obtained, where regardless of anodic dissolution time there was no trace of a Cu_2O reduction wave, while in the -0.55 V vicinity a copper precipitation reaction was observed. The sharpness and deepness of the wave (peak) of this copper precipitation is due to the generated copper powder loosely attached to the electrode surface.

Furthermore, in another confirmatory experiment, Millipore filter paper [d] was fixed on fresh mirror-like surface of pure copper electrode tightly and without gaps between the electrode surfaces (hereafter called MP-paper), and then this MP-paper was fitted with a coarse gauze to act as an artificial slime layer; this so-called "simulated aged anode" was electrolyzed at 200 A/m^2 under the same conditions as in the previous experiment. When this anode became passive at 48 minutes, the artificial slime layer was immediately peeled off, and examination showed that among the large quantity of copper powder produced or copper sulfate salt precipitated, a recognizable amout of Cu_2O was observed on the surface of the electrode. Also, when active electrolysis was carried out on this electrode without being passivated, there was production of copper powder between the artificial slime/anode surface, and no copper sulfate or Cu_2O was observed at all.

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d) Standard paper with thickness of 120 μ, pore size of 1.2 μ, and porosity of 82%.

4. Conclusions

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This study showed that the presence of a Cu_2O phase, which is either contained in the copper electrode system or newly generated, can be easily detected by doing potential sweeps under the appropriate conditions. This electrochemical method appears to be useful when studies of copper anode passivation are to be conducted to correlate with the Cu_2O phase behavior.

From this series of experiments, based on the findings on the cathodic reduction of the Cu_2O phase, the following main conclusions were obtained.

(1) The mechanism of the cathodic reaction of the Cu_2O phase is expressed by the equation $Cu_2O + Cu^{2+} + 2e^- \longrightarrow 2Cu^o + CuO$, in which the copper ion movement toward the cathode surface is dispersion-controlled.

(2) As long as the pure copper anode continues to be the active electrode, the Cu_2O phase is not produced. It is produced only when the anode becomes passive.

(3) By using MP-paper as an artificial slime layer, data on the surface products (Cu^o powder, sulfate salts, Cu_2O, etc) on the pure copper anode during electrolysis were obtained quite readily. This becomes a useful technique for future studies on the passivation of the copper anode from a variety of perspectives.

Finally, we thank the INCO Metals Company, Limited for permitting us to publish this report.

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Table 1 Sample identification.

Sample No.	Oxygen level (ppm)
G 0 (*)	1700
G 1	210
G 2	450
G 3	820
G 4	1300
G 5	1900
G 6	5000
G 7	7200

(*) INCO's anode as received.

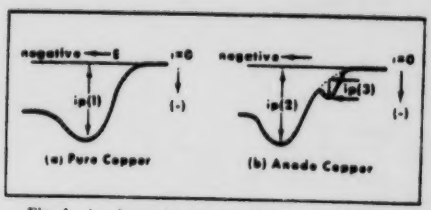

Fig. 1 A schematic representation of cathodic polarization curves of pure and high-oxygen copper in copper electrolyte; At potential sweep rates greater than 0.6 V/min.

Table 2 Analysis of reduction waves indicated in Figure 1.

Anode	Sweep rate $(v/sec)^{1/2}$	E at ip (v)	Kind of ip	Peak current ip (A/cm^2)	$ip/(v(sec)^{1/2}$ $(A/cm^2)(v/sec)^{1/2})$
Pure Cu	0.10	-0.545	ip(1)	0.0878	0.878
	0.130	-0.548		0.1144	0.880
	0.182	-0.552		0.1544	0.848
	0.259	-0.556		0.2233	0.862
	0.316	-0.560		0.2744	0.868
G7	0.10	-0.537	ip(2)	0.0932	0.932
	0.130	-0.541		0.1139	0.876
	0.182	-0.544		0.1701	0.934
	0.259	-0.548		0.2230	0.861
	0.316	-0.552		0.2748	0.870
G7	0.10	-0.413	ip(3)	0.0297	0.297
	0.138	-0.420		0.0399	0.307
	0.182	-0.430		0.0501	0.275
	0.259	-0.436		0.0609	0.235
	0.316	-0.444		0.0698	0.221

	ΔE(mV) for each ten folds increase in V	n from $\Delta E = \frac{30}{n}$ mV
Case of ip(1)	15	2.0
Case of ip(2)	15	2.0
Case of ip(3)	31	0.97

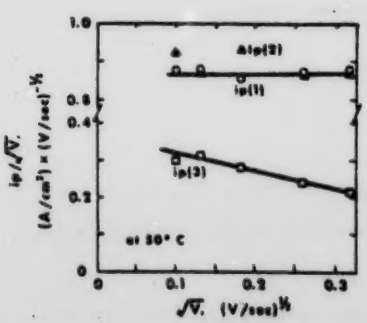

Fig. 2 $ip/\sqrt{V}$ versus $\sqrt{V}$

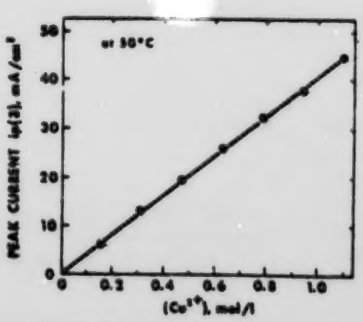

Fig. 3 The relationship between peak current $ip(3)$ and Cu^{2+} ion concentration obtained for copper anode G7.

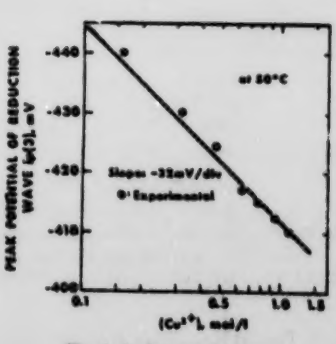

Fig. 4 Peak potential versus $[Cu^{2+}]$ for anode G7.

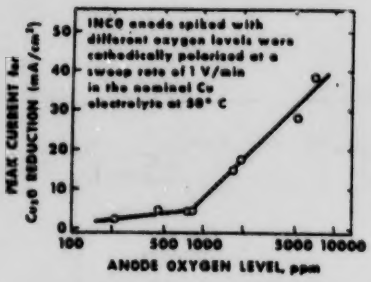
INCO anode spiked with different oxygen levels were cathodically polarized at a sweep rate of 1 V/min in the nominal Cu electrolyte at 65° C
PEAK CURRENT for Cu2O REDUCTION (mA/cm2)
ANODE OXYGEN LEVEL, ppm

Fig. 5 The peak current for Cu_2O reduction which increases with increasing oxygen level in copper anode.

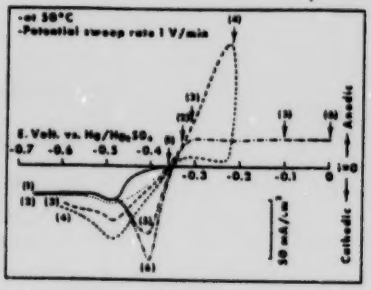

Fig. 6 Potential-sweep polarograms of pure copper showing that the Cu_2O phase forms only when it is passivated.

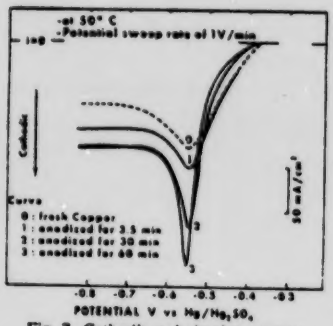

Fig. 7 Cathodic polarization curves of pure copper anodized for different lengths of time at 200 A/m².

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A Mechanism of the Cathodic Reduction of a Cu_2O Phase Present on the Surface of a Copper Anode

—— Anode passivation in copper refining (1st Report) ——

by Shinichiro ABE[1], Sakichi GOTO[2] and Noboru MASUKO[3]

A simple electrochemical method has been established to detect a Cu_2O phase present or newly formed on the surface of a copper anode. Utilizing this technique, a study has been extended to investigate conditions which allow this oxide phase to form during anodization.

A well-defined peak corresponding to the reduction of a Cu_2O phase appears on the cathodic voltammetric curve provided a sufficiently fast potential-sweep rate is employed (i.e., > 0.6 V/min). This reduction reaction proceeds through the following three sequential steps;

$$\begin{cases} Cu_2O + 2e^- \rightarrow 2Cu^\circ + O^{2-} & \text{(electron transfer)} \\ Cu^{2+} + O^{2-} \rightarrow CuO & \text{(rate-determining)} \\ CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O & \text{(following reaction)} \end{cases}$$

The overall cathodic reaction is expressed by,

$$Cu_2O + Cu^{2+} + 2e^- \rightarrow 2Cu^\circ + CuO$$

and its equilibrium potential as calculated from the Nernst's equation based on the present experimental conditions is −0.42 V vs. Hg/Hg_2SO_4, which coincides very well with the experimental value.

Various anodizing conditions were given to a pure Cu anode, and analysis of the results indicates that a Cu_2O phase only forms when the copper anode is passive.

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The Origin of Cu_2O Phase Present in a Layer of Anode Slimes*
- Anode Passivation in Copper Refining (2nd Report) -

by Shin-ichiro ABE[1] and Sakichi GOTO[2]

An electrochemical technique, which has been established previously, was adopted to investigate the origin of a Cu_2O phase often detected in the anode residues in copper electrorefining.

It has been found that a Cu_2O phase in the slime layer originated from the surface of a corroding anode. Therefore, when oxygen content increases in the copper anode, an amount of Cu_2O entering the slime layer correspondingly increases; thus making it thicker. This causes the mass transport of Cu^{2+} ions from the surface of a corroding copper anode to be more restrictive, and, in turn, the tendency of the anode to passivate increases.

Material balance calculations have shown that about 3 to 5% of Cu_2O in the anode enter the slime layers when a large variety of copper anode samples were anodically dissolved under the nominal testing conditions. This ratio was observed to further increase to about 8% when one particular anode sample contained 7300 ppm oxygen.

A Cu_2O phase present in a layer of anode slimes, when contacted with a sufficient amount of oxidizing agent such as dissolved oxygen, is expected to dissolve actively according to the chemical reaction,

$$Cu_2O + 2\,H_2SO_4 + \tfrac{1}{2}\,O_2 \rightarrow 2\,CuSO_4 + 2\,H_2O \quad (\Delta G^\circ = -47.3 \text{ kcal/mol})$$

The addition of a small amount of H_2O_2 to Cu electrolyte increases the oxidizing effect, which agrees with the observed fact that the tendency of anodes to passivate dramatically decreases by this addition as well as by sparging O_2 gas in the electrolyte.

1. Introduction

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If we regard the oxygen contained in crude copper as one of the impurities, its level (generally 1000 - 3000 ppm) is much higher than that of any other impurity.

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If this oxygen exists mainly as Cu_2O phase in the anode parent metal, the percentage formed by this copper oxide reaches up to 0.9 - 2.7wt% and Cu_2O may quite possibly become a potential power which would exert a considerable influence on the physical properties of the slime layer formed.

According to the material balance between the amount of copper dissolved from the anode and that of Cu_2O found in the slimes usually observed in the refineries, the greater part of Cu_2O in the anode copper is electrochemically dissolved and the smaller undissolved part enters the continuously growing slime layer. It is very important to clarify whether 100% of Cu_2O phase detected in the slimes originated from the anode parent metal or whether some reaction took place and produced a certain percentage of the Cu_2O phase.

The anode has the tendency to passivate, which intensifies as the oxygen content in the crude copper increases. It has been previously reported[1] that this tendency was mainly caused by the fact that the slime layer, growing considerably with the increase of oxygen content, becomes thicker and denser. It has been also found that this increase in the amount of slimes formed was mainly due to the gradual increase of the copper components in the slimes such as Cu_2O and Cu^o (a).

In the present report, the origin of Cu_2O phase present in the slimes was studied in reference to the fact established in our 1st report(b), that is to say, no Cu_2O phase is formed as long as pure copper anode continues to dissolve actively. Especially in the case of crude copper, unlike the case of

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(a) When the nickel level in the anode is high, the ratio of NiO phase entering the slimes correspondingly increases.

(b) Journal of the Mining and Metallurgical Institute of Japan, June 1981.

pure copper which does not produce any slime layer, the presence of a slime layer may considerably [illegible] the composition of the solution adjacent to the electrode/slimes from that of the remote solution. We also examined whether or not these particularities[c] due to the adjacency of an electrode can be a favourable condition for the formation of Cu_2O phase in a layer of slimes.

2. Methods of the experiment

The potential sweep method, which has been established in our previous report, was used to confirm the presence of Cu_2O phase in the slime layer produced by electrolyzing a crude copper anode and to compare the relative amount of phase present. Table 1 shows the chemical compositions of the crude copper samples G0 - G7 submitted to a series of experiments carried out in standard copper solution (g/L: 40Cu, 20Ni, 200H_2SO_4) at 50°C.

Table 1 Chemical compositions of INCO anode after spiked with different oxygen levels.

(*) As received.

		Impurity level (ppm)											
Anode	Oxygen	Ni	Pb	As	Sb	Se	Te	S	Fe	Bi	Sn	Au	Ag
G-0(*)	1700	4638	85	45	5	371	49	10	5	23	25	4	352
G-1	210	5000	33	29	2	370	50	8	8	16	23	5	350
G-2	450	5000	25	29	3	360	64	8	18	20	5	5	330
G-3	820	5000	43	25	2	370	49	16	17	14	5	4	400
G-4	1300	5000	80	28	2	380	51	10	20	12	4	5	345
G-5	1900	5000	54	20	3	370	65	9	4	17	4	4	350
G-6	5000	5000	100	22	3	350	48	5	11	17	7	4	400
G-7	7200	5003	80	31	3	340	78	9	17	24	6	4	330

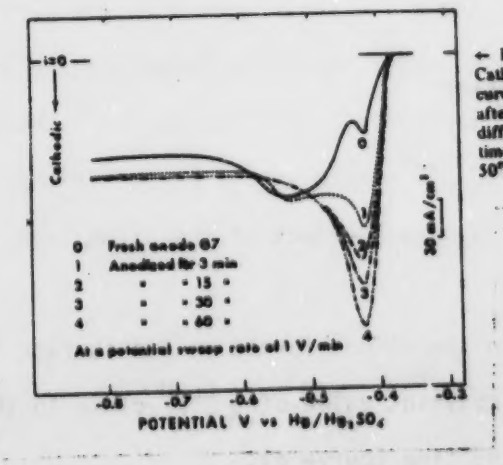
(c) For example, conditions such as high copper ions, low sulfuric acid concentration, etc.

Furthermore, a large piece of INCO crude copper was electrolyzed in addition to the former samples. The slimes formed were washed with water, dried and submitted to chemical and XRD analyses. The main objective of these analyses was to examine material balance of the Cu_2O phase produced.

3. Results of the experiments

3.1. Origin of Cu_2O phase present in a layer of slimes

A crude copper sample with a high oxygen level (O = 7200) was anodized under standard electrolysis conditions for different lengths of time (0 - 60 minutes). Then without wiping off the layer of slimes formed, potential cathodic sweeps were carried out. In each case, a sharp Cu_2O reduction wave was observed around -0.42 V vs. Hg/Hg_2SO_4 (Fig. 1). This reduction current density i_p Cu_2O shows a tendency to increase as anodizing time increases. The increasing rate is very rapid at the beginning and gradually levels off. p 550



← Fig. 1
Cathodic polarization curves of anode G7 after anodizing for different lengths of time at 200 A/m² and 50°C.

Similar reduction waves were observed with all other crude copper samples. Fig. 2 shows the relationship between $i_p^{Cu_2O}$ and anodizing time observed with the sample G1 which has the lowest oxygen level and with the aforesaid sample G7.

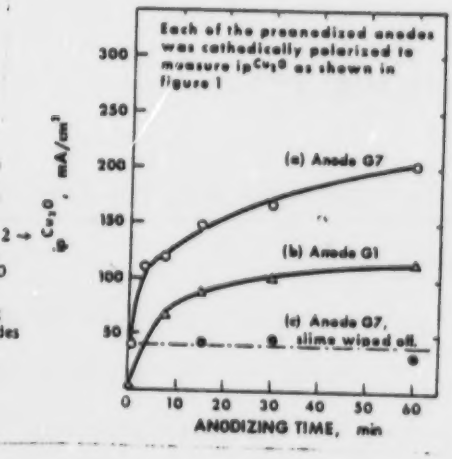


Fig. 2 → Curves showing the tendency for ip^{Cu_2O} to increase with increasing anodizing time of copper anodes with low (G1) and high (G7) oxygen levels.

As was expected, the latter showed a value of $i_p^{Cu_2O}$ much higher than that of the former for all the ranges of anodizing time. The difference is, however, far smaller than the oxygen ratio ($\fallingdotseq 34$) of both samples. As a matter of fact, the ratio of $i_p^{Cu_2O}$ after 60 minutes of anodizing was no more than 2. The following seems to be one of the probable reasons: the slime layer formed on the surface of the anode G7 being considerably thicker and denser than that formed on the anode G1, the diffusion of the copper ions from the distant electrolytic solution to the cathodic surface was seriously inhibited[2]. The $i_p^{Cu_2O}$ ratio should be much higher than 2, if it were not for the diffusion inhibition effect of the slime layer.

The sample G7, when the slimes formed on its surface by anodizing were gently wiped off, showed a constant value of $i_p^{Cu_2O}$ close to the initial value, almost regardless of anodizing time (curve c).

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Summing up the above-stated results, we come to the following inference.

(1) The greater part of the Cu_2O phase in a slime layer is widely distributed in this layer and adheres loosely to the surface of the electrode so that it can easily be wiped off.

(2) The surface of the electrode is dissolved almost uniformly.

The following experiment conducted on the base of inference (1) seems to prove its adequacy.

- passivate the anode G7 for a certain period of time (Fig. 3, process 1f);

- carry out a potential cathodic sweep without wiping off the slimes formed (1b);

- carry out a sweep up to -0.7V beyond the potential where Cu_2O reduction waves appear;

- reverse the scan in the noble direction back to the equilibrium electrode potential (Ee $\doteq$ -0.37V);

- reverse the potential again (2f $\rightarrow$ 2b).

As this CV operation was repeated between Ee and -0.7V (3b,.....), the value of $i_p^{Cu_2O}$ went on decreasing. It practically disappeared at the 4th CV. A similar tendency was observed when the anode G7, instead of being passivated, had only been actively dissolved for a certain period of time (5 minutes). In this case, $i_p^{Cu_2O}$ disappeared at the 3rd CV. A similar CV operation was carried out with the same crude copper electrode having a fresh surface. The reduction wave of Cu_2O disappeared at the 1st cycle (graph b). We suppose that the following process takes place as the CV operations are repeated: while the Cu_2O phase formed and accumulated in the electrode/slimes system gradually becomes exposed and decreases in quantity under cathodic reduction, copper is deposited in the pores of the slimes. As many as 4 CV operations were necessary before the reduction waves

disappeared. This is probably because the Cu_2O phase is widely distributed in this slime layer in a three dimensional manner.

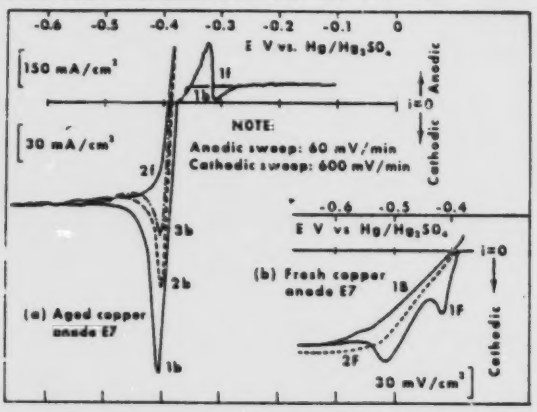

Fig. 3 Cyclic voltammograms of a passivated copper anode.

Judging from the fact that "no Cu_2O phase is produced on the surface of a pure copper anode as long as the anode is actively dissolved" and from the aforesaid CV behavior of the crude copper G7, either actively dissolved or passivated, we can safely say the following. The Cu_2O phase present in the slime formed by the sustained active dissolution of crude copper anode, is derived in part from this parent metal, which was set free. When the anode is passivated, a new Cu_2O phase is produced.

$$Cu^0 \rightarrow Cu^{2+} + 2e^- \quad \cdots\cdots (1)$$
$$E^\circ = -0.3\,V$$
$$Cu_2O + 2H^+ \rightarrow 2Cu^{2+} + H_2O + 2e^- \quad \cdots\cdots (2)$$
$$E^\circ = -0.44\,V$$

(In both cases EV vs Hg/Hg_2SO_4 standard)

3.2. Stability of the Cu_2O phase in the slimes

Will the Cu_2O phase, which moved from the anode parent metal into the slime layers, stay always stable? As the following chemical reaction shows, if one creates conditions allowing a sufficient amount of dissolved oxygen in an acidified copper sulphate* electrolyte from the distant solution and to diffuse and permeate the slime layers, then the chemical dissolution of Cu_2O will be comparatively easy. p 551

$$Cu_2O + 2H_2SO_4 + 1/2\,O_2 \rightarrow 2CuSO_4 + 2H_2O \quad \cdots (3)$$
$$\Delta G^\circ = -47.3\ \text{kcal/mol}$$

In a copper electrolytic cell system, dissolved oxygen is the only oxidizing agent. The dissolved oxygen, though small in quantity, gets started from the distant solution, goes through the slime layer and reaches the anode surface. Its concentration distribution will trace a curve which reaches its peak at the surface between the slimes and the solution, gradually going down deeper into the slimes and coming to the lowest (probably 0 level) at the electrode surface. In other words, the reaction (3) seems to become more active, closer to the solution side. Therefore, the distribution of the Cu_2O phase in a slime layer described in 3.1 may be rather uneven, its concentration being lower on the solution side and higher on the electrode side. In fact, when we wash off carefully with water the black slime layer, which is generally formed on the surface of a corroding crude copper anode, a considerable amount of Cu_2O compound is often found underneath. This compound can easily be removed by more vigorous washing with water.

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* translator's note : literally "sulfuric-acid acidified copper electrolyte"

When electrolysis is carried out in a copper electrolyte whose oxidizing effect was increased, the tendency of the anode copper to passivate decreases dramatically[2]. Oxidizing effect of an electrolyte can be increased by sparging air or O_2 gas in it, or, more effectively, by adding a small amount of hydrogen peroxide. The decrease of the tendency to passivate is probably due to the fact that a considerable part of the Cu_2O in the slimes is oxidized and dissolved by the addition of an oxidizing agent. This chemical reaction progresses most actively at the so-called "dynamic surface" between the copper electrolyte and the slimes which increases continuously. This reaction seems to cause porosity to increase. It means that the effective diffusion route of copper ions from the electrode surface to the distant solution was expanded.

3.3. Particularities of the solution adjacent to the electrode/slimes

The composition of the solution adjacent to the copper anode covered with a slime layer is generally very different from that of the solution far from the anode. The following is a typical composition of the solution collected from the inside of the anodic diffusion layer using a special electrode wrapped in milipore paper just before the appearance of passive state: $[Cu^{2+}]$ = 96 g/L, $[H_2SO_4]$ = 113 g/l and $[SO_4]^T$ = 286 g/l[d]. Such a solution is expected to favor the formation of a new Cu_2O phase. Let us discuss its possibilities. Cu^+ ions, which are dissolved from the entire copper anode surface seem to form Cu^0 powder or deposit Cu_2O through one of the following two processes.

(d) Details will be given in another report. $[SO_4]^T$ is the concentration of the total sulfate radicals.

$$2Cu^{+} \rightarrow Cu^{0} + Cu^{2+} \quad \cdots\cdots (4)$$
$$\Delta G^{\circ} = -8.5 \text{ kcal/mol}$$
$$2Cu^{+} + H_2O \rightarrow Cu_2O + 2H^{+} \quad \cdots\cdots (5)$$
$$\Delta G^{\circ} = -2.3 \text{ kcal/mol}$$

If we compare the standard energy variation of the two reactions, reaction (4) seems to advance much more favourably. However, it does not necessarily deny the possibility of the formation of Cu_2O. As long as there is such a possibility, the conclusion drawn in the previous chapter 3.1, that is, "the Cu_2O phase in in the slime derives from the anode parent metal" is not exact in the strict sense of the term. We can safely say, however, that the greater part of it, if not 100 per cent, is furnished from the anode.

When a sufficient amount of oxidizing agent (dissolved oxygen) is supplied (in other words, the slime layer is thinner and more porous), the copper powder produced in the equation (4) seems to be oxidized and dissolved comparatively easily by the following succeeding reaction.

$$Cu^{0} + H_2SO_4 + 1/2\,O_2 \rightarrow CuSO_4 + H_2O \quad \cdots\cdots (6)$$
$$\Delta G^{\circ} = -41.2 \text{ kcal/mol}$$

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On the contrary, when the slime layer covering the anode is extremely thick and dense, the diffusion and supply of dissolved oxygen and sulfuric acid is inhibited. The copper powder which escaped being oxidized and dissolved, may stay in the slime layer. p 552

3.4. Material balance concerning the formation of a Cu_2O phase

How much Cu_2O from the crude copper anode, escaping from the electrochemical dissolution, enters the slimes and stays there finally? First, large crude copper sample pieces G0 - G7[e] were dissolved under the standard electrolytic conditions. The slimes obtained, washed with water and dried, were submitted to a chemical analysis and X-ray diffraction. Table 2 gives the compounds detected in the slimes by the XRD analysis.

Table 2 XRD analysis.

Compound detected	XRD Analysis(*) G-0	G-1	G-2	G-3	G-4	G-5	G-6	G-7
Cu metallic			C	B	B	B	A	A
Cu_2O		C	A	A	A	A	A	A
NiO	D	C	C	B	B	A	A	A
γ-NiOOH				D	D	D		
$Cu_{2-x}Se$		A	D	D	D	D	C	
UI(**)	A	A	D	D	C	C	C	D
$PbSO_4$								
CuAgSe	C	C	D	D	D	D	C	D
Ag_2Se		D						
Cu_2S	D		D	D	D	D		D
CuS		D		D		D	D	
$6CuO \cdot Cu_2O$	D							
$(Cu_{0.2}Ni_{0.8})O$	D						D	
Cu_2Se	D				D			D
Ag°			C	C	C	D	D	D

(*) A: major phase
B: next major phase
C: minor phase
D: very minor phase

(**) UI denotes unidentified phase.

Fig. 4 shows the variation in slime generation as well as in the copper and nickel components of the slimes in terms of anode oxygen level functions.

(e) 4 x 12 x 1 cm

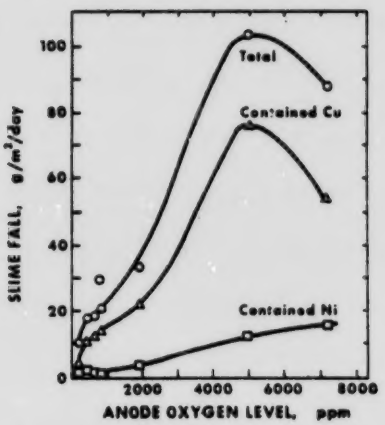

Fig. 4 Slime fall versus anode oxygen level.

From the results of these analyses, it is evident that, with the increase of the anode oxygen level, the slime formation increases remarkably, which is mainly due to the increase of the copper component content. Table 2 shows that copper content consist mostly composed of Cu_2O and, in the second place, Cu^0 powder.

Furthermore, electrorefining test was carried out for several days using a new INCO crude copper sample(f). Material balance of a Cu_2O phase was examined based on the chemical composition of the slimes obtained. The composition of this new sample is close to that of the crude copper G7. (ppm);

O	Ni	Pb	As	Sb	Se
7,300	3,240	27	45	2	410
Te	S	Fe	Bi	Sn	Ag
50	113	17	18	<1	520

(f) The crude copper samples which had been used so far were exhausted.

Material balance was calculated on the following assumptions:

(1) As the nickel level in this sample is outstandingly higher than the other impurity levels, we regard Cu_2O and NiO as the only slime structural components which are bound with oxygen, disregarding other minor impurities.

(2) To estimate the Cu_2O level in the slimes, we first assigned a part of the oxygen content in the slimes to the total nickel content (as NiO), then we formed Cu_2O using the remaining quantity of oxygen. To improve the precision of material balance calculations, the electrorefining test was carried out varying the quantity of sulfuric acid in the standard copper solution from 100 to 225 g/L. The quantity of Ni^{2+} was also varied (0 and 20 g/L).

Table 3 shows the material balance of Cu_2O and NiO phases calculated by the aforesaid method.

Table 3 Balance of Cu_2O and NiO phases.

Electrolyte Comp. (g/l) Cu	Ni	H_2SO_4	Anode C.E. (%)	Slime Fall g/m²/day	Distribution in Slimes, g/m²/day Cu_2O	NiO	Others
40	0	100	105.14	23.77	8.6	7.3	7.9
40	0	150	106.39	24.97	9.2	7.6	8.2
40	0	200	106.40	26.63	10.2	7.6	8.8
40	0	225	106.40	26.98	10.4	7.7	8.9
40	20	100	107.40	28.77	13.2	9.5	6.1
40	20	150	107.60	30.08	14.3	9.3	6.5
40	20	200	107.66	30.96	15.5	10.2	5.3
40	20	225	107.68	32.21	16.9	10.4	4.9

The following assumptions were made to obtain the ratios of these two phases which entered the slimes.

(1) The total amount of Ni in the anode exists in the form of NiO (The quantity of oxygen consumed for the formation of this oxide is expressed by b ppm).

(2) 850 ppm out of a ppm which is the total amount of oxygen in the anode is considered not participating in the formation of either the Cu_2O phase or NiO phase. (This supposition was introduced from the result shown in Fig. 5 in the previous report.)

(3) A Cu_2O phase is formed with (a - b - 850) ppm of oxygen.

The following are the quantities of these phases which were electrochemically dissolved or separated from the dissolving crude copper anode calculated on the above assumptions (Calculations were made using the quantities dissolved when 200 g/l sulfuric acid was added).

quantity of Ni^{2+} added (g/l)	Cu_2O (g/m^2/day)	NiO (g/m^2/day)
0	192.7	24.8
20	195.4	25.1

According to Table 3, about 8% of Cu_2O from the anode parent metal enters the slimes when electrorefining is carried out in the standard copper solution. This value is considerably higher than the typical one (3 - 5%(g)) obtained with industrial crude copper containing a normal amount of oxygen (1000 - 3000 ppm). That the present sample is a high-oxygen level copper may be the reason. The ratio of Cu_2O entering the slimes decreased to 5.3% according

(g) This result was obtained with samples other than INCO crude copper samples. Their compositions being essentially different we are not concerned with them in this report.

to a similar electrorefining test conducted in a similar standard copper solution from which 20 g/L Ni^{2+} had been removed. This is probably because the elimination of Ni^{2+} from the electrolyte relatively decreased a Cu^{2+} in this solution, which caused the equilibrium potential(h) in the equation (2) to move in a baser direction.

Another interesting fact shown by Table 3 is that nickel in crude copper is liberated in the slime at a high entering ratio as is the case with Cu_2O. The ratio observed in normal electrolytic operations is at most 5%(3). This experimental fact seems to be very important with regard to persisting studies on anode passivation in copper refining. Nickel impurity in crude copper keeps its metallic properties as long as the anode oxygen level is low. Consequently, it is in a state easy to be anodically dissolved. As the oxygen content increases, these metallic properties are gradually lost, while the formation of NiO with refractory properties is promoted. This oxide is both chemically and electrochemically very stable. This is probably the reason why such a high penetration ratio was shown. In this case, naturally, the slime membrane formed becomes still thicker and p 553 denser so that it would seriously inhibit the diffusion of copper ions dissolved from the surface of the anode.

4. Summary

The following are the conclusions drawn from the discussion held in the present study.

(1) The greater part of Cu_2O contained in the crude copper anode is electrochemically dissolved into the distant electrolytic solution, while the smaller remaining part (normally 3 - 5%) enters the slimes.

(h) $E = E^{o} + 0.064 \log a^{2}Cu^{2+}$

(2) The greater part of the Cu_2O phase detected in the slimes is formed by the process described in the conclusion (1). Virtually no Cu_2O seems likely to be newly produced in the slimes in spite of the particularities of the composition of the solution adjacent to the anode/slimes (high Cu^{2+}, high* sulfuric acid concentration).

(3) The ratios of Cu_2O and NiO phases entering the slimes increase strikingly with the increase of the anode oxygen content. This makes the slime layer thicker and denser, which is undesirable from the viewpoint of the prevention of passivation.

(4) The addition of an oxidizing agent (dissolved oxygen, H_2O_2, etc.) to the copper solution has the effect of preventing passivation. Its mechanism was discussed.

We wish to thank INCO Metals Company, Limited for allowing us to publish the present study.

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* Translator's note: It seems inconsistant with the foot note (c).

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A Mechanism of $CuSO_4$ Salt Formation on the Surface of a Passivating Copper Anode

—— Anode passivation in copper refining (3rd Report) ——

by Shinichiro ABE[1] and Sakichi GOTO[2]

A proposed mechanism leading to precipitation of a $CuSO_4$ salt on the surface of a passivating copper anode was discussed.

A special technique has been developed to facilitate extracting an electrolyte sample from inside the anode diffusion layer at any given time of anodization, and it has been shown that an electrolyte extracted near the onset of passivity typically contains (g/l) 96 Cu, 18 Ni and 113 H_2SO_4. The concentration of H_2SO_4 assayed here is represented, in the greater part, by HSO_4^-.

In such a highly concentrated electrolyte in terms of Cu^{2+} and HSO_4^- ions, the stability of hydrated $Cu(H_2O)_4^{2+}$ ions near the surface of a passivating anode may gradually decrease, and in its place the following sequential substitution reactions become more predominant;

$$Cu(H_2O)_4^{2+} + HSO_4^- \rightarrow Cu(H_2O)_3(HSO_4^-)^+ + H_2O \quad (1)$$

$$Cu(H_2O)_3(HSO_4^-)^+ + HSO_4^- \rightarrow Cu(H_2O)_2(HSO_4^-)_2^\circ + H_2O \quad (2)$$

and so on.

The productant in equation (2) is presumed to be a weakly associated ionic pair, which autodecomposes when its concentration exceeds a certain critical point, like

$$Cu(H_2O)_2^{2+} \cdots\cdots (HSO_4)_2^{2+} \rightarrow CuSO_4 + H_2SO_4 + 2H_2O \quad (3)$$

to produce $CuSO_4(s)$, H_2SO_4 and some water. The water molecules discharged through this process seem to play a key role in redissolving the precipitated $CuSO_4$ salt while Cu^{2+} and HSO_4^- ions are newly supplied to this site of reaction to be ready for the subsequent process (2) to reoccur. Thus a certain cyclic relation is predicted to build up between the processes (2) and (3) at a near-saturation state of the electrolyte near the passivating anode.

Electrolyte properties at a saturated state were also thoroughly reviewed to support the possibility of this proposed model.

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1. Preface p. 35

Frequently in the course of investigating copper anode passivation characteristics a curve of anodic polarization potential versus time is plotted under a fixed current density load in order to determine time elapsed until passivation occurs. Sometimes an oscillation phenomenon is observed just prior to the onset of passivation (i.e., just before this curve rapidly ascends). The occurrence of this oscillation wave is generally explained as something equivalent to a process where the coating of oxides is ruptured and restored repeatedly on the electrode surface.[1) 2)]

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However, when the facts of a previous report[3], namely, that "it is fundamental to the formation of copper oxide coatings that they lead to a passivation condition of the copper anode" are applied to the above argument some inconsistencies are seemingly apparent.

In this present study the chemical equilibrium which leads to copper sulfate salt layer formation was studied, taking into consideration copper electrolyte as one type of strong electrolytic solution, as well as special conditions where high concentrations of copper and sulfate ions and the like may materialize near copper electrode surfaces during dissolution. Results obtained were then tested for association with the causes for the occurrence of oscillation waves.

2. Experiments and Results

2.1 Conditions for Occurrence of Oscillation Waves

A series of electrolytic experiments were carried out using the current regulation method with a copper solution (55°C) in order to determine under what conditions copper anode generates oscillation waves and to derive a possible generalization. Materials used for the anode were pure copper and a variety of crude coppers; all anodes were polished with #600 grit emery paper, washed, exoleated and used immediately in the tests. Results obtained divided roughly into a few experiment examples which are given below.

Experiment 1: Pure copper + saturated copper solution.

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Standard electrolytic solutions [a] were saturated by added overabundances of copper sulfate, sodium sulfate, etc. Pure copper anodes (4 cm x 4 cm x 1 cm) were electrolysed in these at a standard current density of 200 A/m². In each of the saturated copper solutions oscillation waves occurred regularly on anode potential versus time curve. Repeating a rather slow up-down oscillation, their amplitude gradually increased, until after 3 - 10 min a movement towards full-scale passivation was observed.

Experiment 2: Pure copper + artificial slime layer

The exposed surface area of a pure copper anode was limited to 2.5 x 3 cm² by embedding in epoxy resin. A series of Millipore filter papers [b] (hereafter, MP paper) with pore sizes ranging widely from 0.22 to 8 μ were firmly attached as artificial slime layers. These so-called "simulated aged anodes" were loaded each with differing current densities of 200, 300 and 400 A/m², and a series of dissolution experiments was carried out in the standard copper electolyte solutions. In Table 1 are collected the results obtained concerning oscillation wave occurrence, time of passivation (tp) and anode potential at the first oscillation. From these it was found that oscillation waves tend to occur more easily as the current density is lowered and as the pore size of the artificial slime layer is greater. By and large also, the anode potential at first oscillation wave p.36

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a) Composition (g/l): 40 Cu + 20 Ni + 200 H_2SO_4.

b) Product of Millipore Corp.: standard article layer thickness 120μ, porosity about 82%.

showed values lower than 0.13 V vs. NHE and much lower even than the typical passivation potential (-- 0.4 V); this is exceedingly interesting. In other words, even though the anode is still within the active dissolution potential range the oscillation phenomenon occurs. When an electrode which was in the middle of the oscillation phenomenon was rather rapidly removed from the cell and the MP paper was peeled away from its electrode surface, it was observed that copper sulfate mixed with fine copper powder had been deposited. The formation of copper oxides such as Cu_2O film or CuO was not observed at all.

Experiment 3: Crude copper with differing quantities of oxygen contents

A series of dissolution tests was carried out using specimens [c] of INCO crude copper that had been re-dissolved in the laboratory, and whose oxygen contents were prepared by graphite reduction or by addition of Cu_2O powder over a wide range from 210 - 7,200 ppm. According to results of our previous report[3] the thickness and denseness of the slime layer obtained through electrolytic refining of crude copper using such differing oxygen levels increases together with oxygen levels. First, each specimen (4 cm x 12 cm x 1 cm) was electrolysed for 20 hours in standard electrolytic solution using a current density of 200 A/m², causing formation of a slime layer. Subsequently the current density was raised to 400 A/m² and its electrode potential versus time curve were followed. The appearance or absence of

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c) Same as anode specimens used in the previous report.[3]

oscillation waves are summarized in Example 1 of Table 2. As is apparent from the Table, oscillation waves tend to appear more readily with low oxygen copper.

Next, anodes which did not produce oscillation waves in the above experiment (G3, G4 and G6) were given similar anode treatment by variously changing concentrations of copper electrolyte over a 20 hour period, in order to investigate tendencies for occurrence of oscillation waves.

Copper electrolyte concentration was prepared by changing the added amounts of sulfuric acid from 100 to 225 g/L. In this crude copper anode treatment test it was anticipated that anode slime forming from the same specimens would become denser as the sulfuric acid concentration increased.[5] As can be seen from the results shown in Example 2 of Table 2, oscillation waves appeared (in G3 and G4) when the amount of sulfuric acid added was brought to 150 g/L or lower. The reason anode G6 did not become susceptible to oscillation waves in this experiment as well may be that it already contained too much oxygen and had a too thick layer of slime formation.

Experiment 4: Various kinds of crude copper.

A total of 12 kinds of crude copper[4] furnished from 9 copper refineries received anodic treatment for 20 hours beforehand in the same manner as Experiment 3. Then, with current density raised to 400 A/m² a series of oscillation wave occurrence tests were carried out. There were various crude coppers, some producing oscillation waves and others not producing any, etc.; Fig. 1 illustrates several examples of anode potential versus time

curves which show this. As can be seen from this figure, generally at the moment when passivation begins to occur the anode potential abruptly rises to 10 V and over. When the direct current power source unit was kept fully opened to its greatest allowable impressed current (24 V), the potential began soon to decrease; going through a irregular variation process, it settled to a potential value which appeared to be seemingly stationary. This stationary potential is referred to here as reactivation potential (E react); its values vary greatly with the type of crude copper. p.3

When E react values are plotted against tp (Fig. 2), it becomes apparent that oscillation waves show a tendency to appear more in specimens that had smaller E react values. It was observed that the easier a crude copper reverted to reactivation the more severe was the rupture and separation brought on during passivation by the slime layer covering its surface. This appears to suggest that the adhesive condition of this slime to the electrode surface is rather loose.

Now, when anode G5 which had a fresh surface was electolysed immediately at 400 A/m² without prior anodic treatment oscillation waves appeared. By way of contrast, passivation was markedly speeded up, and completed without any time left for oscillation waves in a similar experiment carried out with MP paper attached to this specimen's electrode surface.

From results of Experiments 1-4 given above, the following matters are considered important as conditions for the appearance of oscillation waves.

(1) Oscillation waves are a phenomenon that appears given the appropriate conditions irregardless of pure copper or crude copper;

consequently there is no direct connection with the characteristics of the anode itself.

(2) As oscillation waves appear at a potential under that at which oxides form on the surface of the copper anode, they do not correspond directly to such processes whereby layers of oxides repeatedly rupture and restore themselves.

(3) Rather, it is probably a phenomenon which appears under physical influence from a slime layer forming on the anode surface--particularly, thickness, porosity and adhesion to the surface. Oscillation waves appear more readily as the slime layer is correspondingly more porous.

(4) The oscillation wave phenomenon may have a close correlation with some kind of saturated solution equilibrium at the electrode interface since oscillation waves appear when its solution environment is put into a saturated condition even with pure copper which does not form a substantive slime layer.

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2.2 Occurrence Mechanism of Oscillation Waves

2.2.1 Composition of Solution Near Anode.

If, as stated in Conclusion (4) of section 2.1 above, the oscillation wave phenomenon is attributable to peculiarities in the state of the solution near the electrode just prior to passivation, then it would seem to be important to know clearly the make up of the solution.

So a special copper anode was manufactured as shown in Fig. 3. Changing conditions of solution composition were investigated at various points in time from anode treatment time 0, through the oscillation process, up to passivation. The electrode used here was pure copper (2.5 cm x 3 cm) that had been embedded in epoxy; two semipherical openings (0.95 cm ø) were made on its surface. Then this epoxy substrate and the entire electrode were firmly attached by MP paper (1.2 μ). This was placed vertically in the copper solution and electrolysed at 200 A/m^2. After carrying out anode treatment for each electrolysis time (6 , 12 & 20 min: oscillation in progress, 22 min: passivation), the test electrode immediately was pulled out of the cell and placed in a watch glass which had been filled beforehand with hot water to a level where the lower half of the horizontally placed electrode would be submerged. Next solution was drawn out of the interiors of the two semipheres by thrusting an injector through the artificial membrane while preventing the re-crystallization of copper sulfate. Amounts of 0.2 - 0.28 mL of solution drawn from inside this so-called diffusion layer (called here for convenience "anodelyte") were diluted immediately to make all the contents 25 mL Using chemical analysis, concentrations of copper ions, nickel ions and sulfuric acid were determined.

In Fig. 4 are shown results when 20 g/L Ni^{2+} was added and not added to the test solutions. According to this, while Ni^{2+} ions decreased only very slightly from the initial concentration, the concentration of Cu^{2+} ions from inside the diffusion layer increased steadily up to 96 g/L at oscillation onset

(about 19 min). During this time, the concentration of sulfuric acid fell to roughly half (113 g/L) the concentration in solution removed from the electrodes. Cu^{2+} ion density sank to 79 g/L 22 min after passage through oscillation and development of passivation. This was due to formation of copper sulfate salts on the electrode surface. By contrast, in cases where Ni^{2+} ions were not added, solubility of copper sulfate salts increased because the total salt concentration of the test solution fell accordingly. Consequently, the density of Cu^{2+} ions near the electrode reached 115 g/l and 28 min later oscillation began. In addition, there was a far longer oscillation period than in the case of the Ni^{2+} ions-added solution: after 38 min passivation finally started. Also it was observed in all tests that as the oscillation phenomenon proceeded copper sulfate being deposited on the copper anode gradually spread over thickly.

2.2.2 Measurement of Anodelyte Vapour Pressure.

A synthetic solution of the same composition as the anodelytes obtained at each of dissolution times of 0, 6, 12, 20, and 22 min in 2.2.1 above was prepared. Vapour pressure measurements were carried out at 55°C. Results are given in Table 3. At the start of electrolysis solution vapour pressure showed 95 mm Hg; this increased as electrolysis proceeded. This overall increase in vapour pressure is thought to be caused by predominant p.3 scattering speeds of free sulfuric acid due to the electrophoretic force from the anodelyte, with a certain gradual increase in Cu^{2+} ion concentration near the electrode . While Ni^{2+} ions and sulfuric acid concentration in the anodelyte appeared to have reached generally steady values after

12 min of electrolysis, Cu^{2+} ion concentration continued to further increase, causing a drop in vapour pressure until 19 min later oscillation waves started. And half way through oscillation, at 20 min, vapour pressure showed a minimum of 100.5 mm Hg. This fact indicates that oscillation starts when solution near the electrode becomes most concentrated. After passing through the oscillation process, at the point of copper anode passivation, the vapour pressure again rises. This is because the number of mols of free water in its vicinity has increased as a result of precipitation of copper sulfate salts.

2.2.3 Precipitation Model for Copper Sulfate Salts.

Copper ions in copper electrolytic solution seem generally to assume the form of $Cu(H_2O)_4^{2+}$ hydrated ions. Most likely the concentration of copper ions in solution near the copper anode progressively heightens during the progress of electrolysis, and total sulfate ions (SO_4^{2-}, HSO_4^-) gradually increase as well. There is probably room for discussion as to whether under these special solution conditions hydrated copper ions can be present, maintaining their forms intact, stable and unchanged. In a solution where total sulfuric acid ion density rises very high the equilibrium of the SO_4^{2-} / HSO_4^- ion system probably settles down so that HSO_4^- ion formation becomes much more predominant.[6] In this case the present form of copper ions, even while maintaining unaltered their quadridentate configuration, may produce among the HSO_4^- ions, for instance, models similar to the following sequential substitution reaction :

$$Cu(H_2O)_4^{2+} + HSO_4^- \rightleftarrows Cu(H_2O)_3(HSO_4^-)^+ + H_2O \quad \cdots\cdots (1)$$

$$Cu(H_2O)_3(HSO_4^-)^+ + HSO_4^- \rightleftarrows Cu(H_2O)_2(HSO_4^-)_2^0 + H_2O \quad \cdots\cdots (2)$$

The compound which forms in the second step of this model rather than being a coordination compound is perhaps a half association ion $Cu(H_2O)_2^{2+}$ $\cdots\cdots(HSO_4^-)_2$. Considered this way, it is a convenient to explain a process that is effected in a short time whereby the compound autolyzes and sulfates are deposited. d)

$$Cu(H_2O)_4^{2+} \cdots (HSO_4^-)_2 \rightarrow CuSO_4 + H_2SO_4 + 2H_2O \quad \cdots\cdots (3)$$

d) The five water molecules that combine with copper sufate salt are not shown in the formula.

At the same time when copper sulfate salts are precipitated 2 mols of water are liberated as well. As explained below, this is probably the important point of the model equation above. In other words, it is obvious that just after passing through reaction (3) oscillation begins: once copper sulfate salts have precipitated onto the copper anode, they do not stay there long, but rather redissolve. As this copper salt precipitates the entire electrode surface soon becomes completely covered with this coating and inconveniently this does not contribute to the oscillation phenomenon but rather leads directly to transition to passivation. Thus copper sulfate salt once having precipitated in an exceedingly small amount redissolves after a limited time has passed. At that time it is thought that water molecules liberated in reaction (3) are useful in accelerating this redissolving reaction. It is assumed that this precipitation/redissolving process corresponds to 1 cycle of oscillation.

Now, while this copper sulfate salt is in progress of redissolving, copper ions are continuing to be supplied from the copper anode surface at a fixed rate. Simultaneous with this, new HSO_4^- ions which migrate from solution beyond the immediate vicinity of the anode come into semi-association with these copper ions and complete the preparation for the next stage of copper sulfate precipitation. This process is equivalent to the process whereby concentration polarization gradually increases. This fact can be seen in the scheme in fig. 5 which illustrates typical oscillation waves observed in this study; here the rising part of the each cycle wave (a), which is thought to correspond to this process, shows a comparatively gentle rise. And at the point where this wave form reaches its peak, copper sulfate salt is formed anew and at the same time

concentration polarization is relaxed to a certain extent. It appears that this process (reaction (3)) is completed in an instant and anode potential drops vertically (c). Even while this sort of oscillation wave cycle is repeating itself over and over again, solution concentration near the electrodes gradually increases. As a result, while concentration polarization is rising adequately, the anode potential is gradually drawing nearer to passivation potential. At the moment where oscillation wave growth reaches full maturation its amplitude occasionally reaches even 200 - 300 mV.

In addition, as stated in Experiment 2 of 2.1 above, if the loaded current density is too high, oscillation waves do not appear, even when the copper anode is of the same type, and even when the slime layer on those anodes is of the same form. This is explained as follows: Since the dissolution speed of copper ions from the anode increases correspondingly, all copper ions dash toward any available water near the electrode. As a result there is no margin for the cyclic process of reaction (2) $\rightleftarrows$ (3) to happen, and the electrode is covered with a copper sulfate coating. The same kind of effect also may be brought about if the slime layer is too thick or too dense. (Experiment 3). p.39

2.2.4 Phase Variations of Saturated Copper Solution.

Assuming the reaction model given in the previous sections concerning copper sulfate precipitation, here one prediction becomes possible. Namely, assuming that in a saturated copper solution a substitution reaction progresses consecutively between hydrated copper ions and HSO_4^-, some kind of phase variation is brought on in this solution that corresponds to the respective substitution processes. In addition, this

kind of phase variation can be anticipated first of all to be reflected in some kind of form within parametres such as solution density, viscosity and solubility of copper sulfate.

Results of variations in solubility of copper sulfate in copper solution as a function of amount of sulfuric acid added and measured at 50^{o}, 55^{o} and 60^{o} are given in Fig. 6. All solubility curves while keeping a similarity to each other decreased as sulfuric acid concentration increased. It should be noted here that all curves bend at a specific point of sulfuric acid concentration. The equilibrium equation $CuSO_4 \rightleftarrows Cu^{2+} + SO_4^{2-}$ alone cannot be given as an explanation for this fact. Some sort of phase variation is assumed to have occurred. Looking at the $55^{o}C$ solubility curve, concentrations of copper ions and sulfuric acid at the break in the curve are 95 g/L and about 115 g/L respectively. This almost exactly corresponds to the typical composition of anodelyte at the point of oscillation onset already given in Table 3.

Next, based on the above experimental results, the correlation between ionic products [e] versus $[SO_4]^T$ was computed as shown in Fig. 7. From this graph phase variation appears to happen across all levels (0 - 300 g/L) of added sulfuric acid. Solution composition at point P, with sulfuric acid at about 110 g/L and total sulfuric acid ions at about 280 g/L closely matched that of anodelyte at the point of oscillation onset.

Changes in density and viscosity of saturated copper solution versus dependency on sulfuric acid concentration are shown in Fig. 8. As well, these results seem to indicate the possibility of phase variation.

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e) $[Cu^{2+}] \times [SO_4]^T$

Further, as amounts of sulfuric acid were increased from 0 to 125 g/L, both curves drop sharply. This is thought to be due to gradually increasing HSO_4^- ions in this saturated solution through the reaction $SO_4^{2-} + H_2SO_4 \rightleftarrows 2HSO_4^-$. In other words, the structure of the solution progressively changes. When this dropping phenomenon reached the smallest point (P) its sulfuric acid concentration was close to that in the anodelyte described above.

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3. Results.

The chief conclusions derived from this study are as follows:

(1) The origin of occurrence of oscillation waves is not in the rupture and restoration of copper oxides which form on the copper anode. Rather, it is a phenomenon which happens in response to an equilibrium reaction in the copper sulfate precipitation process that is formed when solution composition near the electrode surface approaches a saturated state.

(2) Oscillation waves do not have a direct relation to anodic characteristics themselves, but rather are greatly influenced by physical properties of the slime layer.

(3) In order to explain the oscillation wave occurrence mechanism and copper sulfate precipitation process, the existence of semi-association ions $Cu(H_2O)_2^{2+}$ .... (HSO_4^-) is postulated.

40

(4) A method was established to collect solution from within the anode diffusion layer during electrolysis by combining specially prepared copper electrodes and MP paper. With this method, solution composition near the copper anode before and after occurrence of passivation was measurable with high precision.

Finally, our thanks go to INCO Metal Company, Ltd. which permitted publication of this study.

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Table 1 Conditions for the oscillation phenomenon to occur

(Note) An anode used here is pure copper (2.5 x 3.0 cm), the surface of which was firmly masked with an artificial slime layer of Millipore filter papers with different pore sizes. At 55°C

Pore Size (μ)	C.D. (A/m²)	Oscillated? Yes	Oscillated? No	Passivation Time (min)	Anode Potential at Oscillation (V vs. N.H.E.)
0.22	200	O		111	0.08
	300		O	14	
	400		O	3	
0.45	200	O		130	
	300		O	21	–
	400		O	5	
0.65	200	O		157	0.10
	300		O	28	
	400		O	8	
0.80	200	O		190	
	300	O		40	–
	400		O	12	
1.2	300	O		31	0.105
	400	O		13	
5.0	300	O		46	0.11
	400	O		22	
8.0	300	O		45	0.13
	400	O		19	

Table 2 A search for various conditions for the oscillation to occur.

(Note) All the measurements were conducted at a C.D. of 400 A/m² and at 55°C.

Example 1: Using a sample of INCO anode spiked with different O levels.

Anode	O Content (ppm)	Slime fall (kg/t Cu)	Oscillated? Yes	Oscillated? No
G0	1700	7.62		O
G1	210	1.65	O	
G2	450	2.97	O	
G3	820	3.36		O
G4	1300	3.01		O
G5	1900	5.48	O	
G6	5000	17.17		O
G7	7200	14.50		O

Example 2: Using some of the above anode samples in Cu electrolyte containing various amounts of H_2SO_4.

$[H_2SO_4]$ (g/ℓ)	Oscillated?, for the anode of G3 Yes	G3 No	G4 Yes	G4 No	G6 Yes	G6 No
100	O		O			O
150	O		O			O
175		O		O		O
200		O		O		O
225		O		O		O

Example 3: Using anode G5 with different surface conditions.

Surface condition	Oscillated? Yes	Oscillated? No	Passivation time (min)
- fresh surface (A)	O		128
- (A) + artificial slime layer		O	~7

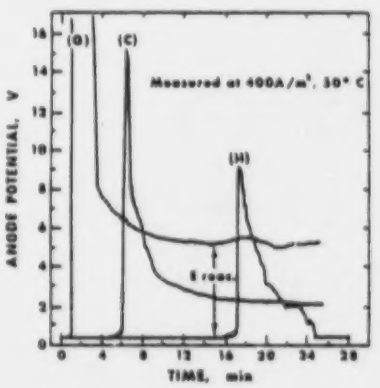

Fig. 1
Typical anode potential versus time curves obtained for aged (*) anodes C, G and H.
(*) Aged for 20 h at 200 A/m², prior to polarizing each aged anode at 400 A/m².

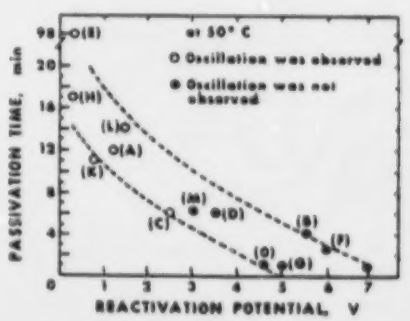

Fig. 2
A plot of passivation time versus reactivation potential obtained for various copper anodes.

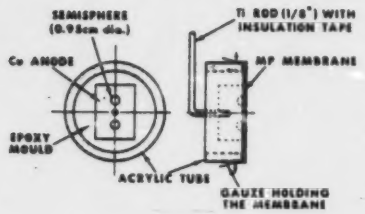

Fig. 3
A simulated copper anode with an artificial slime layer (MP).

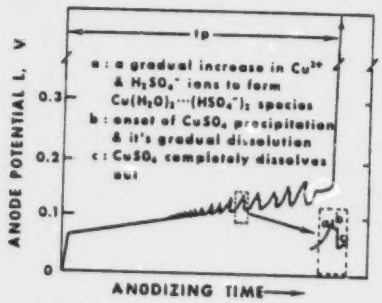
tp
a : a gradual increase in Cu2+ & H2SO4- ions to form Cu(H2O)2···(HSO4-)2 species
b : onset of CuSO4 precipitation & it's gradual dissolution
c : CuSO4 completely dissolves out
ANODE POTENTIAL E, V
ANODIZING TIME

Fig. 5 A schematic representation of typical oscillating waves observed in this study.

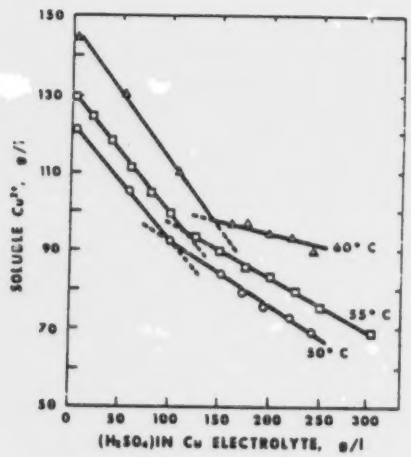

Fig. 6 Solubility of $CuSO_4$ in a system Cu^{2+} – 20 g/l Ni^{2+} – H_2SO_4.

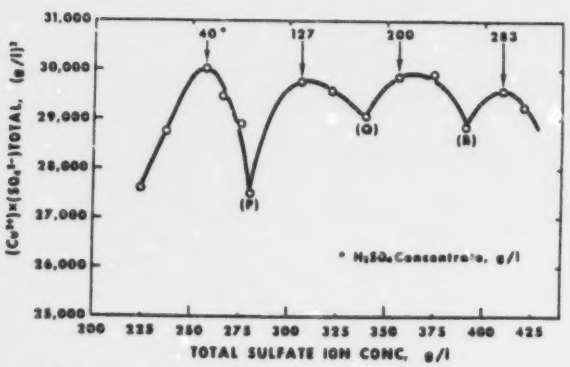

Fig. 7 Ionic product versus $[SO_4]$ total obtained for a saturated copper solution containing various amounts of H_2SO_4(55°C).

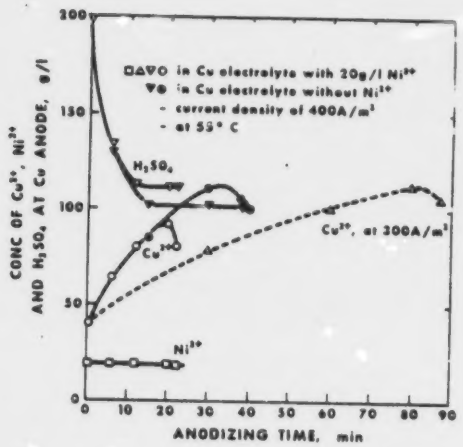
□△▽○ in Cu electrolyte with 20g/l Ni2+
▼● in Cu electrolyte without Ni2+
- current density of 400A/m2
- at 55° C
H2SO4
Cu2+, at 200A/m2
Cu2+
Ni2+
CONC OF Cu2+, Ni2+ AND H2SO4 AT Cu ANODE, g/l
ANODIZING TIME, min

Fig. 4 Composition of electrolyte within anode diffusion layer.

Table 3 Change in vapor pressure of anodelyte (*) with anodizing time.

*: This term was conveniently named to designate the electrolyte within anode diffusion layer.

At 55°C

Sample Number	Anodizing time (min)	State of anode surface	Anodelyte composition (g/ℓ) Cu^{2+}	Ni^{2+}	H_2SO_4	$T\text{-}SO_4$	Vapor pressure (mm Hg)
0	0	active	40.0	20.0	200.0	289	95.0
1	6	active	64.6	19.5	134.2	261.0	98.0
2	12	active	79.2	18.8	112.5	260.5	102.5
3	20	oscillating	96.2	18.3	113.5	286.4	100.5
4	~22	passive	79.1	18.2	112.7	259.7	102.5

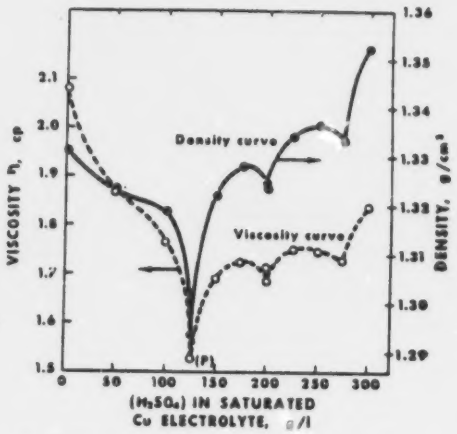

Fig. 8 Viscosity and density curves of a saturated copper electrolyte containing various amounts of sulfuric acid (at 55°C).

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A Mechanism of the Copper Powder Formation on the Surface of an Anodizing Copper Anode

Anode Passivation in Copper Refining (4th Report)

Shin'ichiro ABE* and Sakichi GOTO**

A mechanism leading to the formation of fine copper powder during anodization of a copper anode was extensively studied.

Pure copper samples with different grain sizes and dissolution activities were anodized under various testing conditions in terms of composition and concentration of an anodizing bath, bath temperature and mechanical agitation etc. The measurements of the amount of copper powder formed, its particle size variation and microstructures of the surfaces of corroded anodes have shown conclusively that fine copper powder is formed through the following disproportionating process;

$$Cu^0\ (\text{anode}) \xrightarrow{-e^-} Cu^+ \xrightarrow{-e^-} Cu^{2+} \quad , \ a\% \quad \cdots\cdots \quad (1)$$

$$\text{partially} \rightarrow \tfrac{1}{2}Cu^0 + \tfrac{1}{2}Cu^{2+} \quad , \ b\% \quad \cdots\cdots \quad (2)$$

The earlier theory which explains the powder formation by a mechanical separation of fine metallic copper fragments from the corroding anode could not be supported by our results.

In the proposed model, a% of the total coulombs applied for the anodization is consumed to supply Cu^{2+} ions to the bulk electrolyte while the remaining b% is taken up by the ultimate formation of copper powder. This concept can be expressed mathematically as;

$$\frac{Cu^0 \ (g)}{\text{Anode dissolved } (g)} \times 100 = \alpha \times b \quad (\%) \quad \cdots\cdots \quad (3)$$

where α is the equilibrium constant. In all the experiments, b-value was observed to vary depending upon the testing conditions.

One typical result has shown that copper powder formed in a near-saturated Cu electrolyte decreased its average particle size dramatically to less than 1 micron. This fine particle size is typical for the copper powder which is often detected in a layer of anode slimes obtained in a tankhouse.

1. Introduction

It has often been observed that copper compounds are formed as a structural component of the layer of slimes that is ordinarily produced during

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the electrolytic refining of crude copper. These copper compounds can assume one or more forms, occurring as Cu^0, Cu_2O, CuAgSe, $Cu_{2-x}Se$, etc. Whether these copper components contribute to the creation of a passivated condition to the same extent as do other types of impurities is another issue. Be that as it may, it would seem to be important that we discover what electrolytic reaction process is responsible for the fact that [these compounds]* eventually become stabilized within the layer of slimes. In a previous report[1] the authors investigated the origin of Cu_2O phases that are found within the layer of slimes. Continuing this research, the present paper discusses the mechanism by which copper powder (Cu^0) is formed on the surface of the anode.

2. Experimental Procedures

2.1 Hypotheses Concerning the Mechanism of Copper Powder Formation

Let us first hypothesize that the foregoing Cu^0 powder is produced strictly as a result of one of the following two processes, or possibly as a result of a combination of the two:

(a) A [mechanical] separation reaction

Cu^0 (grain) $\longrightarrow$ Cu^0 (separation, in the form of a powder)

(b) An electrochemical/chemical process

$$Cu^0 \text{ (anode)} \xrightarrow{-e^-} Cu^+ \xrightarrow{-e^-} Cu^{2+} \quad \text{(a charge-migration process)}$$

$$Cu^+ \xrightarrow{\text{partially}} 1/2\ Cu^0 + 1/2\ Cu^{2+} \quad \text{(a disproportionating reaction)}$$

If process (a) were to be the principal factor leading to the formation of the copper powder, we could probably expect that experiments on the dissolution of copper would produce the following results:

(a-1) Some degree of continuity would be observed between the size and shape [of the grains] of copper anodes that possess assorted grain sizes and

*Translator's note: Brackets indicate inferences.

the size and shape [of the grains] of the copper powders that would be formed through their dissolution.

(a-2) Since we can expect that, in a dissolution test, the dissolution of the copper would invariably proceed on the basis of an anodic reaction*

$$Cu^0 \longrightarrow Cu^{2+} + 2e^- \quad \text{(as an overall reaction)} \quad \ldots\ldots\ldots\ldots (1)$$

any increase beyond 100% that might be calculated for the anodic current efficiency using this basic formula would have to have been entirely attributable to mechanical separation.

If, on the other hand, we were to assume that process (b) is the major factor responsible for the formation of the copper powder, we would have first found that both of the lines of thinking that were discussed above [for process (a)] proved to be untenable, and we would probably expect the following results to be observed:

(b-1) is thought to represent the case where the anodic current efficiency exceeds 100% in a given dissolution experiment as a result of a factor other than that represented by the main anodic reaction (1) - the case, that is, where some monovalent, dissolved Cu^+ ion is consumed, not during the charge-migration process, but through the following disproportionating reaction:

$$2Cu^+ \longrightarrow Cu^0 + Cu^{2+} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Therefore, in cases where a% of the total coulombs applied for the anodization from an external source is consumed by reaction (1) and the remaining b% of the coulombs (a + b = 100%) is consumed by the reaction that generates Cu^+ the magnitude of this so-called b-value will be directly controlled by the amount of copper powder that is produced. Furthermore, if

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*Morioka[2)]** and Bockris[3)]**, among others, have suggested that this is a two-stage, one-electron process.

**Translator's note: Inference. The text here states "Bockris[2)] and Morioka[3)], but the reverse order is listed in the References.

this b-value is observed to respond sensitively to changes in a variety of factors - for example, the composition of the anodizing bath, the bath's temperature, the extent of mechanical agitation, the addition of oxidizing and complexing agents, etc. - it can be anticipated that process (b) has probably come to play an increasingly prominent role in the mechanism by which copper powder is formed.

(b-2) If we further extend the concept of the b-value that was introduced in connection with the above hypothesis, we obtain the following relationship:

$$\frac{\text{The amount of copper powder produced (g)}}{\text{the amount of metal dissolved at 100\% C.E. (g)}} \times 100 = b\ (\%)$$

The above relationship would only hold in cases where reaction (2) proceeds at 100% efficiency toward the right. In fact, however, since an equilibrium condition controlled by the rate constants for this equation, $\vec{k_f}$ and $\overleftarrow{k_b}$, would probably be maintained, the above formula should be rewritten as

$$\frac{\text{The amount of copper powder produced (g)}}{\text{the amount of metal dissolved at 100\% C.E. (g)}} \times 100 = \alpha \cdot b\ (\%)$$

$$(0 < \alpha < 1)$$

The left-hand side of the equation, i.e., the part dealing with the rate of copper powder formation, will be provisionally referred to as "the degree of powdering".

As was discussed above, the authors conducted a series of dissolution experiments in which they tested [whether] processes (a) and (b) [can account for the copper-powder formation that is observed on the surfaces of anodizing copper anodes]. Employing [different types of] pure copper as the anodes in this study, the authors observed how, among other things, the b-values, the degree of powdering, and the size and shape of the [grains of the] resulting copper powder varied when the electrolysis was performed under different conditions.

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2.2 Dissolution Experiments

Five different types of pure copper anodes (electrolytic copper, cathode copper, cold-rolled copper exhibiting a 93% degree of rolling, annealed copper, and tempered copper) - which means, therefore, anodes that exhibited /p. 38 different grain sizes and dissolution activities - were each dissolved in a copper electrolyte for approximately 24 hr at 200 A/m^2 and 55° C. The Cu^0 powder that was produced was then collected from the surface of each of the anodes and from the bottom of the electrolytic bath, and it was weighed after being rinsed with water and dried. The grain sizes of the copper powders were determined at this time, and the microstructures of the surfaces of the corroded anodes were also observed.

The electrolytic cells that were employed in these experiments had different capacities, i.e., 500, 1,000 and 3,000 mL. The anodes (surface areas 0.5 - 3 dm^2) were placed at the centres of these cells, and stainless steel negative plates were positioned at their sides. With the exception of a few special cases, the anodizing bcth was not mechanically agitated. Moreover, to ensure that none of the copper powder that was produced in the dissolution experiments would be lost through [migration] to the cathode, a box type of negative plate* was utilized to keep the [cathode] isolated from the anode. The copper electrolyte used in the experiments was a composite solution that essentially consisted of 40 g/L of copper mixed [into] 200 g/L of H_2SO_4. A number of different foreign metal ions (Na^+, Ni^{2+}, Al^{3+}, etc.) were added in suitable [amounts] to this basic solution before the experiments began.

Finally, we can note that copper anodes frequently become corroded at the gas-liquid boundary during the dissolution process. Since mechanically

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*Translator's note: Inference; literally, the text says a "cathode box".

separated constituents of the anodes should not be allowed to become incorporated in the copper powder that forms [as a result of the anode's dissolution], the copper anodes were kept stabilized throughout the experiment by a titanium rod covered with insulating tape, the rod being screwed into the upper part of the anode. The entire anode, so equipped, was immersed in the test solution when the dissolution experiments were being conducted.

3. Experimental Results

A series of dissolution experiments were carried out under a variety of conditions (altering the composition of the anodizing bath, the bath's temperature, and the current density, or adding complexing agents, etc.). The results that were obtained in these experiments are discussed below from several different standpoints.

3.1 The Shape and Size of the Grains of the Cu^0 Powders Formed in the Experiments

First of all, the shape of the grains of the copper powders that were obtained throughout the dissolution experiments was not entirely continuous with that of the grains of the parent material from which the copper anode was made. Figure 1 shows the microstructures of the corroded surfaces of annealed copper and cold-rolled copper, as well as the typical shapes of the [grains of the] Cu^0 powders that were produced from the anodes composed of them. As a rule, [the grains of] these copper powders were potato-shaped, and their size usually fell within the 5-20 μ range. The particle sizes noted for the parent materials, however, were much larger than this. What is more, observation of the microstructures of the corroded surfaces of the anodes indicated that the dissolution of the anodes had proceeded locally along grain boundaries; that is, there was absolutely no support for the possibility that grains that had not yet been completely dissolved may have instead broken off mechanically or

been "gouged out", so to speak.

3.2 The Effect of the Composition of the Anodizing Bath

If hypothesis (a-2) in Section 2 above were to be true, we would expect that a Y = X relationship would be obtained between the amount of copper powder that was formed and the amount that represented an increase over the extent of anodic dissolution occurring when [the current efficiency] exceeds /p. 39 100%.* A number of dissolution experiments were carried out after various types of foreign metal ions had been added to the basic copper solution in different amounts. The data that were obtained in these experiments, however, exhibited a rather wide, irregular distribution far below the straight line that would be expected if the foregoing hypothesis were true (Fig. 2).

Figure 3, meanwhile, shows the values for the degree of powdering that were calculated on the basis of these experimental data as a function of the b-values. From the plot shown in this figure, it is evident that the coefficient gradually changed from 1/2 --> 3/4 --> 4/4. If we now examine in greater detail the results appearing in Fig. 3, we find that the b-values displayed a conspicuous increase with increasing concentrations of the foreign metal ions in the copper electrolyte (Fig. 4), and a similar increase was also detected for the amount of Cu^0 powder that was formed (Fig. 5). On the other hand, a tendency was observed for the average grain size of the copper powder to become gradually finer as the concentration of the copper electrolyte increased. Figure 6 shows a typical example of how the particle size of the copper powder changed when nickel ion was added to the basic copper solution in various amounts ranging between 0 and 40 g/L. The addition of the nickel ions had the most pronounced effect on the degree of powdering, whereas the addition of

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*$\Delta W \times (\text{anode C.E.} - 100)/100$ (ΔW: amount of anodic dissolution)

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sodium ions had the least effect.

A tendency similar to that described above still occurred even when the concentration of free sulphuric acid in the copper electrolyte was increased. However, the variation in the grain size of the Cu^0 powder became much more marked under these conditions, especially when the $[H_2SO_4]$ concentration was higher than 200 g/L, when a sharp increase was observed in the fineness of the particles. On the other hand, when the NH_4^+ radical - a radical which can be expected to produce a stable complex ion with the monovalent copper ion - was added* in the form of ammonium sulphate to the copper electrolyte, which already contained 10 g/L of the Ni^{2+} ion, a dramatic increase in the degree of powdering was observed (Fig. 7).

3.3 The Effect of Using a Saturated Copper Electrolyte

When copper is electrolysed under real-life conditions, Cu^0 powder is formed through some process or another in such a way that the powder comes to exist within a layer of slimes that continuously grows thicker. However, since a layer of slimes can generally be found in the vicinity of the electrode at the time this Cu^0 phase is being produced, the composition of the /p. 40 anodizing bath generally will change to the point where it has a very high concentration of Cu^{2+} ions and sulphur ions (HSO_4^-, SO_4^{2-})4). Accordingly, for this study the authors carried out a series of dissolution experiments using copper electrolytes in which the Cu^{2+} ion concentration varied between 0 and 75 g/L (i.e., near the saturation point). The results of these experiments suggested a number of points, which will now be discussed.

(1) The b-values showed a tendency to gradually decline as the concentra-

*The amount added was equivalent in terms of ion strength to the amount of the Ni^{2+} ion that was added - i.e., 10 g/L. Therefore, when [such an amount of ammonium sulphate] is added, the copper electrolyte will exhibit the same ion strength as it exhibits when 20 g/L of the Ni^{2+} ion is added.

tion of the Cu^{2+} ion increased; in fact, near the saturation point these b-values rapidly approached 0%. Moreover, a similar tendency was observed for the variations in the degree of copper powder formation (Fig. 8). These findings are believed to be attributable to the fact that the equilibrium in the disproportionating reaction (2) slipped more toward the left side as the concentration of the Cu^{2+} ions increased.

(2) On the other hand, the particle size of the copper powder that was formed tended to become gradually finer as the Cu^{2+} ion concentration increased. In fact, near the saturation point, the particles exhibited an abrupt decline to a size of only 1 micron. A highly interesting point to note here is that the particle size that was observed [under these experimental conditions] resembled the average particle size of Cu^0 phases that have been encountered in anode slimes under actual operating conditions. A typical example of this is shown in Fig. 9 (the copper phase is revealed by the bright areas in this figure).

(3) Two dissolution experiments were carried out in saturated copper solutions. In the first of these experiments, the electrolysis was more or less forcibly continued for 24 hr, under conditions such that periods of passivation alternated with periods of active dissolution while a high current density load of 400 A/m^2 was being applied. In the second experiment, on the other hand, the electrolysis was conducted for a 24-hr period while employing a standard current density of 200 A/m^2 and keeping [the anode] in a non-passivated condition*. In both of these experiments, the corroded** surface [of the anode] bore a close resemblance to the smooth surface that is observed after

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*A so-called "current interruption" was applied in this instance, allowing the electric current to flow in the forward direction for 3 hr and then breaking off the current for 10 min.

**Translator's note: Inference; the text says "dissolved surface".

the slimes have been removed when copper is electrolysed under ordinary conditions.

(4) In the first of the two experiments discussed in Section (3) above, it was observed that a greyish-white precipitate had formed on the surface of the passivated, pure copper anode*. When this electrode was shaken backwards and forwards in the solution while the same level of current was being applied, some of this precipitate fell away from the electrode's surface, and before long it was observed to move away from the electrode and dissolve into the solution. This phenomenon is thought to have arisen as a result of [one of] the following chemical reactions:

$$Cu_2SO_4 + H_2SO_4 + 1/2\ O_2 \longrightarrow 2\ CuSO_4 + H_2O \quad \ldots\ldots\ldots\ldots (3)$$
$$(\Delta G^0 = -31.9 \text{ kcal/mol})$$

Or:

$$Cu_2SO_4 \longrightarrow CuSO_4 + Cu_0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$
$$Cu_0 + H_2SO_4 + 1/2\ O_2 \longrightarrow CuSO_4 + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$
$$(\Delta G^0 = -41.2 \text{ kcal/mol})$$

Furthermore, when the passivated anode to which this precipitate had become attached was taken out of the electrolytic cell, the area on the electrode's surface that came into contact with the air almost instantly turned brown. When, however, the same operations were performed using an anode that was identical except for the fact that it had not undergone passivation, this change to a brown coloration began to occur only after a considerable period of time had elapsed, and the brown colour that eventually appeared was not as rich or dark.

Judging from the experimental results noted above, it would appear that the monovalent dissolution of copper anodes and the equilibrium [point] in the

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*Translator's note: As it was difficult to collect this precipitate from the anode, the authors were unable to make a phase identification. They believe, however, that it may have been Cu_2SO_4.

subsequent process of copper powder formation are significantly influenced by the concentration of Cu^{2+} ions in the anodizing bath.

3.4 Influence of the Temperature of the Anodizing Bath

Another series of dissolution experiments were carried out using standard copper electrolytes* at temperatures ranging from 43° C (the saturation temperature for copper sulphate in this type of solution) to 70° C. /p. 41 The results of these experiments are shown in Fig. 10. As the data in this figure clearly indicate, both the b-values and the degree of powdering tended to increase with an increase in the anodizing bath's temperature. The latter values, however, suddenly levelled off once the temperature surpassed 60° C, falling below the expected values**. On the other hand, the particle size of the copper powder that was formed became more and more coarse as the anodizing bath's temperature rose. At the present stage of our research, it is not entirely clear why the degree of powdering was observed to be related to the bath temperature in these experiments. The authors' suspicion, however, is that the value for the coefficient α declined below 0.5 because some of the copper powder that was produced during the tests had been leached out by the acid in the course of the anodization, or perhaps because some sort of intrinsic change took place in the process of copper powder formation when the electrolyte's temperature reached 60° C.

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*Those electrolytes were prepared by adding 20 g/L of Ni^{2+} to the basic solution that was employed in this research.

**Based on the data that are shown in Fig. 8, the value of α, a coefficient for the degree of powdering (which = $\alpha \cdot b$), works out to approximately 0.5 for temperatures below 60° C. It was hypothesized that the α coefficient would continue to exhibit this value at temperatures above 60° C.

4. Discussion

Summarizing the results that the authors obtained in the above series of dissolution experiments utilizing pure copper anodes, there would seem to be much stronger support for the theory that the copper powder appearing on the surfaces of the anodes was formed by means of process (b) than there is for the theory that it was produced by process (a). Now the equilibrium constant K for the disproportionating reaction (2) that leads to the formation of Cu^0 is given by $K = a_{Cu^{2+}}/a^2_{Cu^+}$. Although the quantity a_{Cu^+} in this equation can obviously be changed by directly altering the concentration of Cu^{2+} ions in the anodizing bath, it is also thought that the addition of foreign metal ions, etc., can bring about a corresponding change in this quantity, too. This is because each of the foreign metal ions (Na^+, Ni^{2+}, Al^{3+}, etc.) that is added to the electrolyte possesses its own inherent hydration number. For example, the Ni^{2+} ion, which stabilizes by taking up six water molecules, probably caused a greater reduction in the number of moles of available water in the copper solution than did the addition of the Na^+ ion, which has a lower hydration number. Therefore, when each of the foreign metal ions was added to the electrolyte in an amount that would provide the number of moles appropriate for it, a greater reduction in the amount of available water would have been caused by the addition of the Ni^{2+} ions than by the others, and a corresponding increase would have occurred in the value of $a_{Cu^{2+}}$. In fact, the b-values and the values for the degree of powdering that were observed in the present study behaved in a manner that seems to support an explanation along these lines (Figs. 4, 5).

A similar type of real variation in the value of $a_{Cu^{2+}}$ can, of course, be brought about by adding to the copper solution an ion - for example, NH_4^+ - that demonstrates a good ability to form complex ions in combination with copper ions. Since some copper ions are aminated by the addition of $(NH_4)_2SO_4$,

the equilibrium in reaction (2) is believed to have shifted toward the right, leading to the sharp increase in the degree of powdering that is indicated by the results in Fig. 4.

Increasing the concentration of sulphuric acid in the copper electrolyte also caused an increase in the b-values and the degree of powdering. Experimental data that provide a valuable comparison with these were obtained in a separate study that the authors conducted[5]. That is, if the concentration of sulphuric acid in the copper solution is gradually increased during the electrolysis of crude copper, then the total amount of slime that is produced will tend to show an increase, even though the anode will become more sensitive toward passivation. Furthermore, the fact that the Cu^0 phase that exists within [this slime layer] also is gradually augmented has been confirmed by X-ray diffraction data. These experimental findings appear to have very important implications, suggesting that greater attention and concern should be given to measures that can prevent the occurrence of [anode] passivation when industrial decisions are being made to determine what volumes of sulphuric acid will be added to copper electrolytes.

The experiments in which saturated copper solutions were employed yielded highly interesting results concerning the degree of powdering that developed and the particle size variation of the copper powder. This sort of behaviour seems to be closely related to the existence of very high concentrations of copper ions near the surface of the copper anode during the electrolysis process (Fig. 8). When, pursuing this line of thinking further, additional dissolution experiments were carried out under different stirring conditions, the results indicated that there was a greater degree of copper powder formation in the stirred solutions than in those that were not subject to

mechanical agitation (Fig. 11*). This finding is thought to indicate that the stirring had reduced the concentration of copper ions in the vicinity of the electrode, and this was the same type of tendency as was discussed in connection with the data in Fig. 8.

When the Al^{3+} ion was added to the copper electrolyte, it became hydrated, and this in turn led to a corresponding increase in $a_{Cu^{2+}}$. Moreover, the addition of this Al^{3+} ion increased the viscosity of the solution, and this made the state of the Cu^{2+} ions' dispersion worse. The results shown in Fig. 5 are thought to reflect the overall effects that were attributable to the addition of this ion.

It is a general empirical principle of chemistry** that "the particles of a powder become finer as the rate of the powder's chemical formation increases, and, conversely, the particles become coarser as the rate of the powder's formation becomes slower." Now, the results that were obtained in the present study can be considered to show a tendency similar to that indicated by the above principle, since the degree of powdering (which is to say, the rate of the copper powder's formation) was observed to increase as the concentration of the anodizing bath increased, while at the same time the particle size of this powder gradually became finer. (See Fig. 6.)

When oxidizing agents were added to the copper electrolyte, it is believed that an oxidizing reaction involving the transformation $Cu^{+} \longrightarrow Cu^{2+}$ came to take precedence over the disproportionating reaction (2), whose rate is thought to be relatively slow. This [oxidizing reaction] can be presumed to have brought about a decline in the degree of powdering. A striking increase was

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*In this case it was necessary to measure only the anode C.E. This value can be presumed to be a reflection of the extent to which the degree of powdering itself varies.

**The reduction of hydrogen can be cited as another example [of such a general empirical principle].

noted in the dissolution activity of crude copper in a copper electrolyte to which a small volume (3-5 mL) of H_2O_2 had been added. Similarly, when air or O_2 gas was blown in, the copper anode showed less of a tendency to become passivated. Table 1 presents the results of additional experiments that were carried out along these lines. According to the data in this table, the degree of powdering dropped off markedly as oxidizing agents with greater oxidizing power were employed. Moreover, it appeared obvious that there was also a pronounced decline in the tendency for the crude copper to become passivated.

It is widely known that when a copper anode is fixed vertically while an ordinary type of electrolysis is being performed, the surface of this copper anode will rapidly dissolve, proceeding in a top-to-bottom direction. One of the reasons for this is believed to be that the current density becomes unevenly distributed as a result of the development of what has been aptly described as a "concentration distribution" in the solution (that is, the solution becomes more concentrated toward the bottom), this variation arising on account of convection. In addition to this, however, there may also be another explanation for this top-to-bottom dissolution, as the results of the present experiments indicate that the upper parts of the copper /p. 42 [anode] undergo a more active monovalent dissolution.

5. Conclusion

Experiments were performed in which pure copper anodes were dissolved under a variety of electrolysis conditions. Summarizing the results of these experiments, we obtained the following major conclusions.

(1) The copper anode dissolves on the basis of a two-stage, one-electron reaction. A very small amount of the Cu^+ ion that is dissolved in this manner is believed to participate in a subsequent disproportionating reaction that produces copper powder. It is unlikely that the formation of this copper

powder arises as a result of mechanical separation from the copper anode.

(2) The above two processes - i.e., the monovalent dissolution of the copper and the disproportionating reaction that follows - are strongly influenced by the conditions of the electrolysis. The parameter of the b-value was introduced as a means of [setting] a criterion that would enable us to understand the rate of the foregoing reactions. It was found that these b-values sensitively reflected variations in the anodizing bath's composition, the bath's temperature, stirring conditions, the current density, and so forth. In the authors' view, this parameter can play a significant part in helping us gain an understanding of the mechanism by which copper anodes dissolve, including the mechanism of copper powder formation.

Finally, the authors are indebted to the INCO Metals Co., Ltd., for granting them permission to publish this research.

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FIGURES AND TABLE

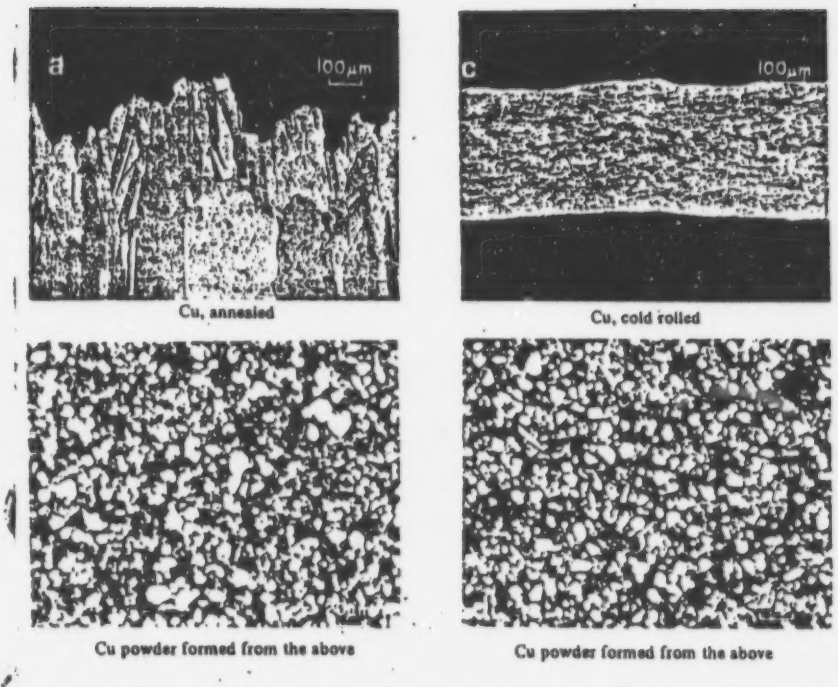


Fig. 1 Typical photomicrographs showing copper powder formed on the surfaces of corroding copper anodes.

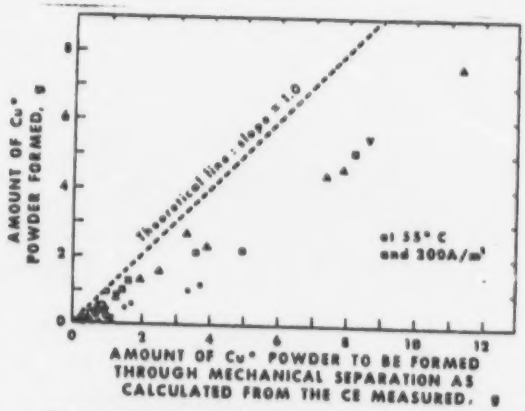

AMOUNT OF Cu⁺ POWDER FORMED, g
theoretical line : slope = 1.0
at 35° C
and 200A/m²
AMOUNT OF Cu⁺ POWDER TO BE FORMED THROUGH MECHANICAL SEPARATION AS CALCULATED FROM THE CE MEASURED, g

Fig. 2 A plot of anodic dissolution data for various types of pure copper.

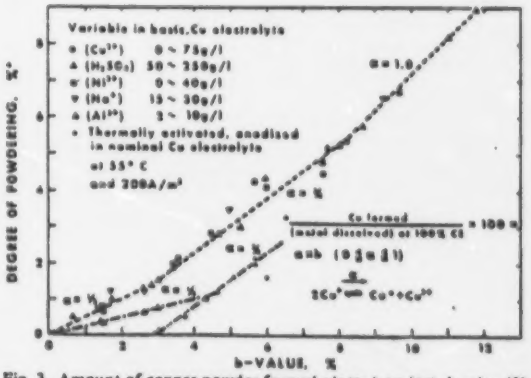


Fig. 3 Amount of copper powder formed plotted against b-value (°).

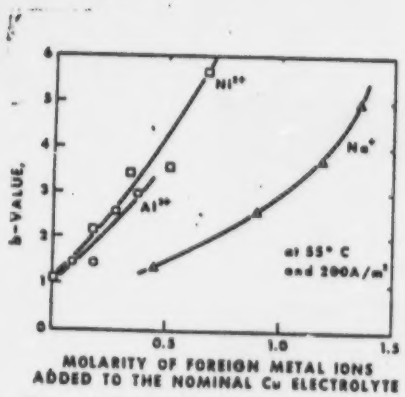


Fig. 4 Curves showing the tendency for b-value to increase with increasing concentration of copper electrolyte.

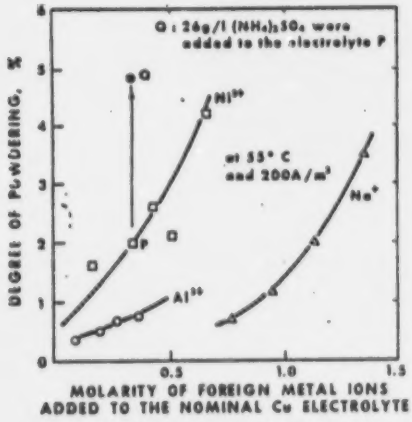


Fig. 5 Curves showing the tendency for degree of powdering to increase with increasing concentration of copper electrolyte.

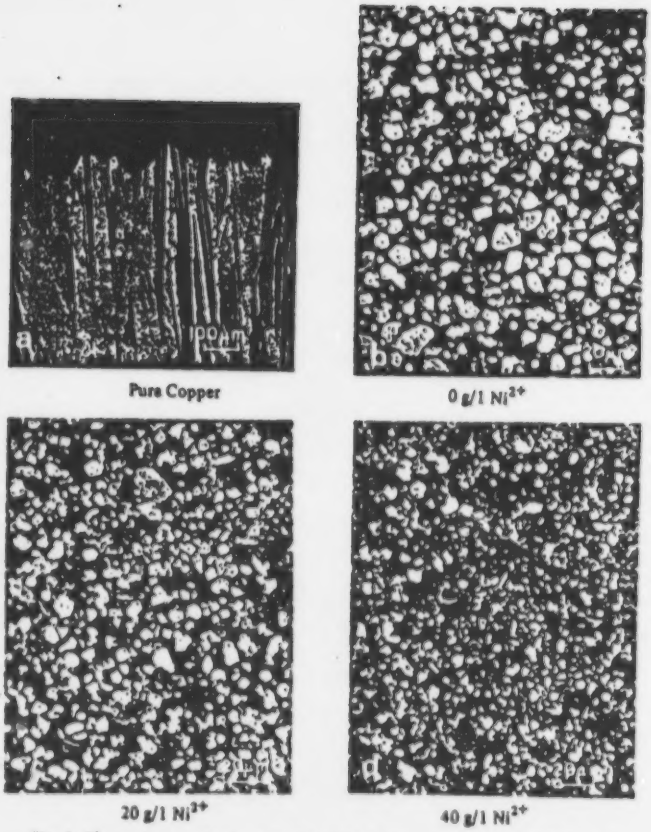


Fig. 6 Photomicregraphs showing the effect of electrolyte concentration on particle size of copper powder formed on the surface of an anodizing copper.

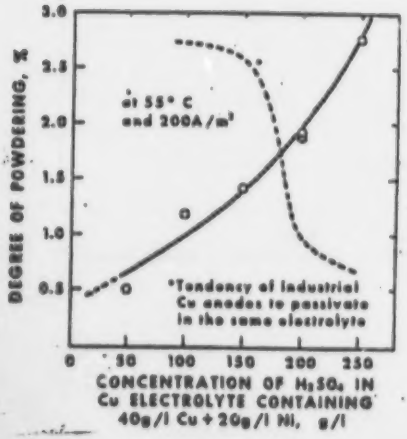


Fig. 7 Degree of powdering versus acid concentration.

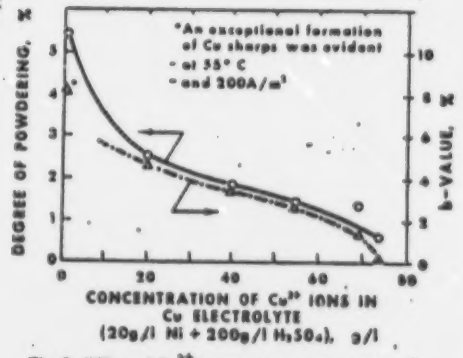
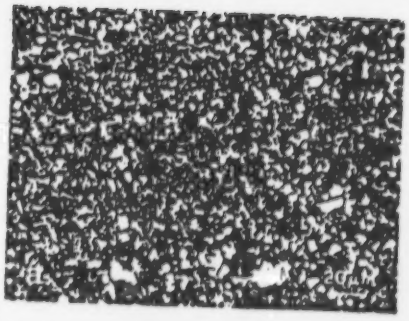


Fig. 8 Effect of Cu^{2+} ion concentration on the mechanism of copper powder formation.

a) Copper powder derived from pure copper in a Cu solution (75 g/l Cu, 20 g/l Ni and 200 g/l H_2SO_4).



b) Copper powder (bright spots) derived from INCO anode copper (E 11)

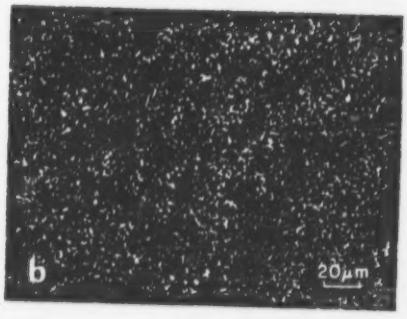


Fig. 9 ... conditions; (1) in a saturated copper solution and (2) in anode slimes at 200 A/m²

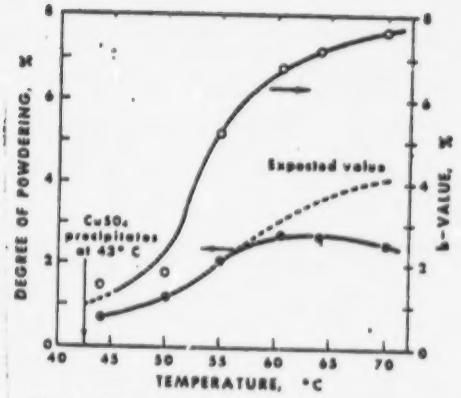


Fig. 10 Effect of electrolyte temperature upon the mechanism of Cu powder formation.

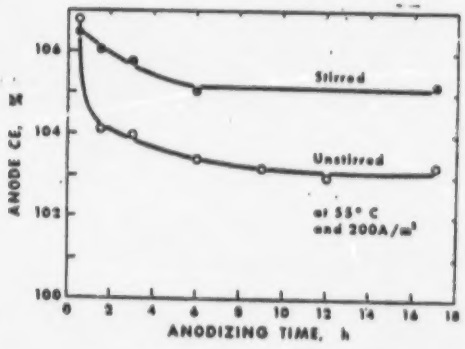


Fig. 11 Effect of stirring the electrolyte upon the current efficiency for dissolution of copper anode.

Table 1 Effect of oxidizing agent

At 55°C

	Oxidizing agent employed to Cu electrolyte:				
	N_2 Sparging	As it is	Air Sparging	O_2 Sparging	H_2O_2 (5 mℓ/ℓ)
– t_P(sec) of INCO anode measured at 1000 A/m²	80	120	170	245	>1000
– Degree of powdering obtained for pure Cu at 200 A/m², (%)	6.8	5.5	4.9	2.7	0.5

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EFFECT OF ANODE OXYGEN UPON PASSIVITY OF COPPER ANODES---ANODE PASSIVATION IN COPPER REFINING (5th REPORT)---

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Effect of Anode Oxygen upon Passivity of Copper Anodes*

- Anode passivation in copper refining (5th Report) -

by Shinichiro ABE[1] and Sakichi GOTO[2]

A study was done by means of an electrochemical technique to determine how anode oxygen affects the dissolution activity during electrorefining of copper anodes.

One particular anode material was remelted, and spiked with a wide range of oxygen levels. This set of copper anodes was used to investigate the dissolution characteristics by comparing parameters such as critical anode current density, activation energy and *i*-t decay curve which were measured both at a fresh and aged surface.

The results obtained have shown that,

1) Increasing oxygen level in the copper anodes initially results in an enhancement in the dissolution activity. This beneficial effect, however, is only so when the surface is fresh, and becomes counteracted soon by a layer of anode slimes which tends to grow thicker and denser with increasing oxygen level.
2) When oxygen content increases in a copper anode which already contains a high nickel level, the tendency of this anode to passivate increases drastically. This is due to the formation of refractory NiO during anode casting making the slime layer denser and more restrictive to the mass transport of Cu^{2+} ions away from the surface of a corroding anode.

1. Introduction

In a previous report[1)], the results of a series of studies of passivation using crude copper samples provided by nine electrorefining companies were reported. According to the report, a direct correlation between the distribution of impurities and the passivation characteristics was not found. However, it was observed that, in general, crude copper which produces a greater amount of slime has a tendency to show a stronger receptivity to passivation. The role such slime played in passivation has been also confirmed in the

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2. Regular member, Dr. of Engineering, Prof. Dept. of Metal Engineering, Faculty of Engineering, The University of Tokyo.

experiments which followed[1)2)]. A specified crude copper sample was chosen and the experiments were performed using a set of copper anodes whose oxygen levels were adjusted to encompass a wide range. The results showed that the increase in the anode oxygen level was one of the factors which increased the thickness and density of the slime formed. Ultimately this promoted the passivation of copper anodes.

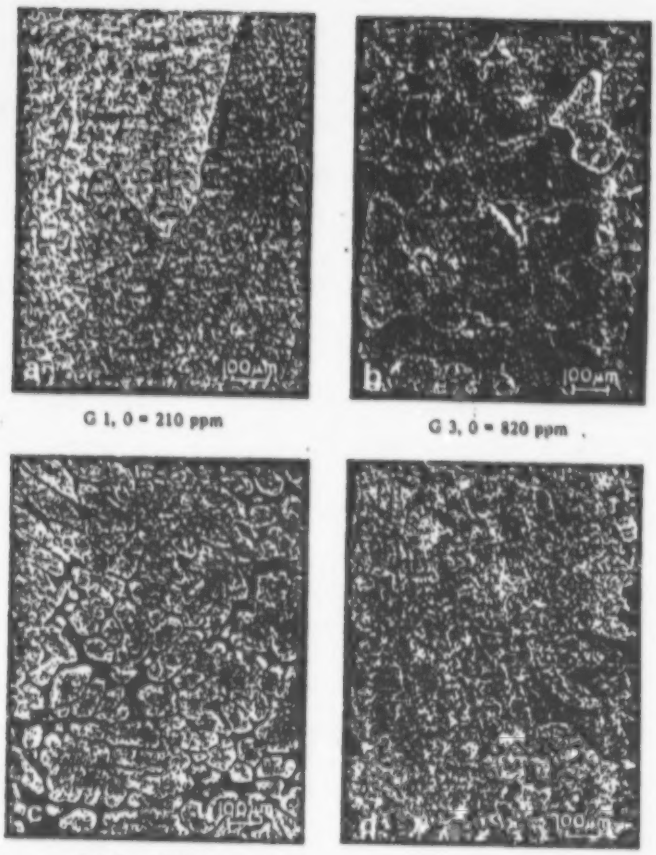
On the other hand, there is a theory that an increase in the anode oxygen level plays a useful role in the reduction of passivation in a tankhouse[3)]. As this is explained later in detail, when the granular crude copper with various oxygen levels was acid leached under vigorous stirring, the dissolution reaction speed shows a tendency to increase as the oxygen level increases. If we consider that anode dissolution and acid leaching are, in essence, a kind of oxidation reaction expressed by $Cu \rightarrow Cu^{2+} + 2e^-$, the claims laid by the industry, as stated above, seem to be justifiable at least superficially.

Thus, in view of the fact that the oxygen level in crude copper has a great effect on the process of electrolysis much more than it has ever been thought to have in the past, the differences in the claims stated above are investigated in this study using mainly an electrochemical technique.

2. Method of experiment

2.1 Anode samples

Crude copper made by INCO Metals Company, Ltd. was



G 1, O = 210 ppm

G 3, O = 820 ppm

G 5, O = 1,900 ppm

G 7, O = 7,200 ppm

Fig. 1 Microstructures of anode G with different oxygen levels.

remelted at the laboratory and the oxygen levels were adjusted to a range of 210–7,200 ppm. After they were allowed to cool, a small sample piece (1.3 x 1.3 x 1.0 cm) was cut from each solidified piece and embedded in epoxy resin. An electrode was made so that its exposed surface area became 1.69 cm^2. The method of sample preparations and the chemical compositions have been already given[2]. Fig. 1 shows the results of the structural observation of several samples prepared.

2.2 Method of experiment

In order to make a phase comparison of activity in the anode dissolution for each sample, the following electrochemical values were measured at 50°C.

(1) Critical current density in the dissolution activity: i_a^{crit}

(2) Activation energy: E_a

(3) Decay curve: i - t curve

Firstly, the surface of each electrode was smoothed down to No. 600 of emery paper, degreased, washed with water and used for experiment immediately. The copper solution used was a synthetic solution with a composition of 40Cu + 20Ni + 200H_2SO_4(g/L). For the polarization measurement, the potential scanning speed was kept at 0.06V/min. The potentiostat used was made by Brinkmann Company (type: SSI 70). This was connected to a voltage scan generator, VSG 72 made by the same company and to a X-Y recorder, 7044A made by Hewlett Packard Company. In this study, the potential was collated with Hg/Hg_2SO_4 electrode unless stated otherwise[a].

p. 1290

3. Results of experiment

3.1 Critical current density

Generally, when a copper anode is polarized from the equilibrium potential to the nobler direction in an acidic copper sulfate solution, firstly, a dissolution activity

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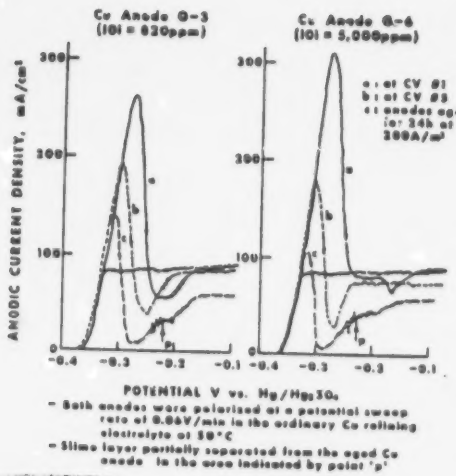
a) +0.64V to the hydrogen standard electrode


Cu Anode G-3
(IOI = 620ppm)
Cu Anode G-6
(IOI = 5,000ppm)
ANODIC CURRENT DENSITY, mA/cm²
POTENTIAL V vs. Hg/Hg2SO4
a : at CV #1
b : at CV #3
c : anodes aged for 24h at 300A/m²
- Both anodes were polarized at a potential sweep rate of 0.06V/min in the ordinary Cu refining electrolyte at 50°C
- Slime layer partially separated from the aged Cu anode in the area indicated by point 'p'

← Fig. 2
Cyclic voltammograms showing the effect of anode oxygen level upon dissolution activity.

occurs. As the potential rises, this anode reaction becomes gradually more active and the corresponding amount of electric current i_a increases until it reaches a certain critical point. The potential which gives this critical current density, i_a^{crit}, is generally called the Flade potential. Beyond this point, the copper anode begins real passivation.

This occurrence of passivation is a phenomenon caused by the coverage of the whole area of the anode surface by the nonconducting copper sulfate film. As a result, the anode potential rises suddenly and a Cu_2O phase is also formed. The speed of formation of this copper sulfate film[b] in a process of copper electrolysis can be represented by the speed of accumulation of copper ions and sulfuric acid ions near the anode surface. It is thought that the accumulation speed

b) $CuSO_4 \cdot 5H_2O$

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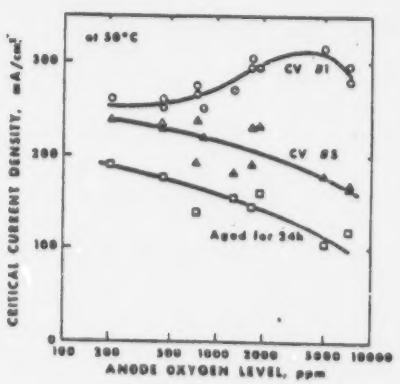

Fig. 3 — Effect of aging upon dissolution activity of copper anode with different oxygen levels.

depends solely on the physical properties (thickness and porosity) of the slime layer formed on the anode surface when the negative current density is constant. That is, the degree of dissolution activity of copper depends not only on its own activity but also largely on how strongly the slime layer can act to prevent the diffusion of copper ions which are leaching out incessantly from the anode surface.

Therefore, the anode polarization was started when each anode had a fresh surface. Then the dependency of i_a^{crit} on aging time was investigated by scanning the potential repeatedly between the equilibrium potential and -0.1V. As the number of scanning of cyclic voltametry (CV) increased, the corrosion of the anode surface progressed and the thickness and the density of the slime layer also increased. As a result, the i_a^{crit} value at the first CV was a maximum and the value decreased gradually as the number of CV increased. It was estimated that as the rate of decrease became greater,

the resistance of the slime film against the copper diffusion also became greater.

Among the results of a series of experiments based on this point of view, the polarization behaviour of copper with low level of oxygen (G3) and that with high level (G6) are given in Fig. 2. The polarization curves in Fig. 2 are those for the first CV, for the fifth CV and for the state in which the anode was aged for another 24 hours at $200A/m^2$ and the slime layer was developed to a thickness of near equilibrium. The change in i_a^{crit} thus obtained was plotted as a function of anode oxygen level and is given in Fig. 3. From these results, it was found that the dissolution activity had a tendency to increase with the increase in the oxygen level as long as the anode surface was fresh. However, when electrolytic corrosion was performed with the same level of oxygen which corresponded to that for the fifth CV, such a positive effect of oxygen disappeared and a contrary effect appeared. When the electrolysis advanced further, this contrary effect became more prominent.

The Flade potential read off the polarization curve for the first CV of the entire electrode sample was about -0.28V. On the other hand, when the pH (o.3) of the solution at a distance from the copper anode is substituted into the following equilibrium potential equation for the Cu_2O phase formation which was changed to this experimental condition, the value obtained was -0.189V and was quite different from the value of the actual

measurement.

$$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^-$$

$$E = -0.17 - 0.064\ pH$$

In order to obtain E= -0.28V, the pH of the solution should be about 1.7. This can be explained in the following from the results of the study given in the previous report[4]. That is, it was found that the solution[c] taken from near the copper anode immediately before the passivation occurred contained 114/96 g/L each of free sulfuric acid and copper ions. A part of the copper ions forms semiassociation ions of $Cu(H_2O)_2^{2+}.....(HSO_4^-)_2$ and the rest maintains the equilibrium relationship expressed by $CuSO_4 \rightleftarrows Cu^{2+} + SO_4^{2-}$. Free p. 1291 sulfuric acid above was formed according to the following equation. It was formed during the process of diluting the sample solution (~0.25 mL) to 25 mL.

$$Cu(H_2O)_2^{2+} .....HSO_4^-)_2 \rightarrow CuSO_4 + H_2SO_4 + 2H_2O$$

In other words, 1.16 mol semiassociation ions existed in this concentrated solution. It is thought that 0.35 mol copper ions were maintaining equilibrium with $CuSO_4$. If we suppose that other free sulfuric acid does not exist alone in this anodelyte, the source which can regulate the pH in the solution near the anode surface may be HSO_4^- (2.32 mol) that is weakly associated with the semiassociation ions. It can be thought that the degree of effectiveness depends strongly on the

---

c) It was named Anodelyte.

Table 1 Degree of partial dissociation of Cu $(H_3O)^{2+}{}_3 \cdots (HSO_4^-)_3$ ions and the resulting solution pH (50°C).

Degree of Dissociation (%)	Effective $[HSO_4^-]$ (mol/ℓ)	Effective $[H^+]^{(*)}$ (mol/ℓ)	Expected pH
100	2.32	0.048	1.32
80	1.86	0.043	1.36
60	1.39	0.037	1.43
40	0.93	0.031	1.51
20	0.46	0.022	1.67
10	0.23	0.015	1.82
5	0.12	0.011	1.97
1	0.02	0.004	2.40

(*) Dissociation constant K; $HSO_4^- \rightarrow H^+ + SO_4^{2-}$ was assumed to be 10^{-3} at 50°C.

degree of association of these ions. Now, for convenience, the expected pH values are given in Table 1 when various proportions of associated HSO_4^- ions took part in the determination of pH. In this calculation, the dissociation constant of $HSO_4^- \rightleftarrows H^+ + SO_4^{2-}$ at 50°C was assumed to be 10^{-3} d). From the results given in Table 1, it is expected that pH= 1.7 should be realized when about 15 % of HSO_4^- ions in the semi-associated ions takes part in the regulation of pH of the solution in some form.

3.2 Activation energy

The relationship between the activation energy and the anode oxygen level was investigated. This parameter is often applied to studies such as the effect of organic additives on copper anode dissolution activity[5)6)]. In this experiment, each anode sample with fresh surface was soaked in the copper solution for testing and was made to reach

d) $K_a = 2 \times 10^{-2}(18°C)$, $1.02 \times 10^{-2}(25°C)$

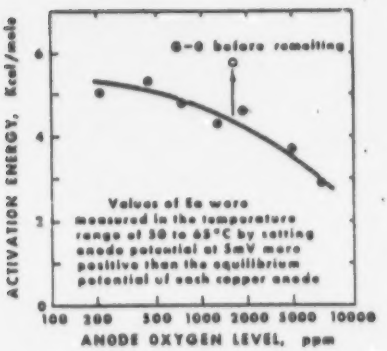
ACTIVATION ENERGY, Kcal/mole
6
4
2
0
G-0 before remelting
Values of Ea were measured in the temperature range of 50 to 65°C by setting anode potential at 5mV more positive than the equilibrium potential of each copper anode
100 200 500 1000 2000 5000 10000
ANODE OXYGEN LEVEL, ppm

Fig. 4 Activation energy versus oxygen level measured for anode G.

the equilibrium potential. Then the dissolution current was obtained after the anode potential was set at 5.0mV above the equilibrium potential. The temperature of solution was set at 50, 55, 60 and 65°C. The dissolution current showed a tendency to decrease with time. Therefore the values where the measured i_a - time curve was comparatively stable (t= 0 ~ several seconds) were read and E_a was calculated from the following equation[7].

$$\log i_a = A - E_a/RT$$

Results are given in Fig. 4. As clear from Fig. 4, E_a value, at a time when the slime layer formed on the anode is almost negligible, tends to decrease with the increase in the oxygen level[e]. The values of i_a when the slime layers became thicker are not given here since they were difficult

e) The reason why the values of E_a for the sample given (G0) tend to be significantly above the curve obtained is under investigation.

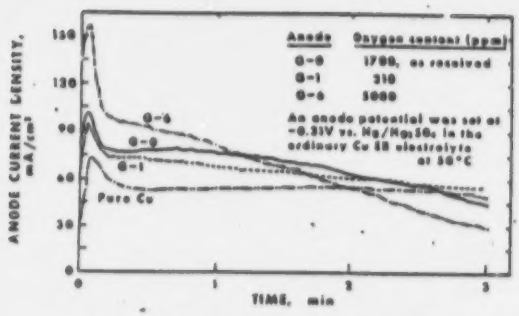

Fig. 5 i-t decay curves; Effect of anode oxygen level.

to reproduce.

3.3 i_a - time decay curve

It has become clear from the experiments performed so far that the anode oxygen which is supposed to give a positive effect is changed to give an opposite effect due to the slime layer. In order to confirm further this fact, the behaviour of i - t decay was observed. Here, copper anodes with a low, a medium and a high level of oxygen (each with fresh surface) were used for dissolution activity at -0.31V and the variation of electrolytic time for i_a was recorded. As given in Fig. 5, as expected, the results showed that the initial anode current increased as the oxygen concentration increased. However, it gradually went through a process of decaying and the order was reversed after 3 minutes of electrolysis. For comparison, the behaviour of decaying for pure copper[f)] was also observed. The initial value of current

f) Anode copper obtained by electrorefining at a laboratory scale was melted under reducing atmosphere and pure copper was produced. Its oxygen content was 90 ppm.

was lower than those of any other crude copper anode. However, it held the initial value almost at a constant as the electrolytic time progressed. i_a value of crude copper G1 decreased below that of pure copper after 10 minutes of electrolysis.

The decay curve for pure copper anode was thought to have reached almost a constant value in the range of 10 minutes of electrolysis. However, if the length of the electrolytic experiment were extended to a day unit, the decay curve should have somewhat decreased further than the level of dissolution current given in Fig. 5. This was assumed from the fact obtained from the following experiment. The pure copper anode was electolyzed for 3 days under a constant current density load (in fact, the constant current method). The anode surface became no longer smooth and showed irregular and severe roughness. It was also observed that the anode potential rose 40~50mV from the initial value as a result of the accumulation of sludge of fine copper powder in the grooves of the corroded surface. Furthermore the phenomenon of reaching the maximum at the initial stage of electrolysis which appeared on the decay curves in Fig. 5 should appear on the anode potential versus time curve in correspondence with the opposite phenomenon of reaching the minimum which would be obtained by changing the constant potential method of this experiment to a constant current method. This has been already observed by UMEZU and others[8] in their study of electrolytic copper

p. 1292

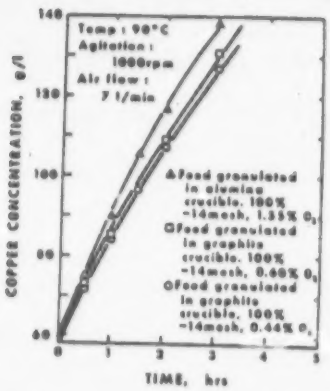
Temp : 90°C
Agitation : 1000rpm
Air flow : 7 l/min
COPPER CONCENTRATION, g/l
TIME, hrs
Food granulated in alumina crucible. 100% -14mesh, 1.55% O2
Food granulated in graphite crucible. 100% -14mesh, 0.60% O2
Food granulated in graphite crucible. 100% -14mesh, 0.44% O2

Fig. 6
Leaching blister copper shot; Effect of using feed batches with different oxygen content.

and copper anodes with the addition of various impurities.

3.4 Acid leaching of granular crude copper

Oxygen was added to crude copper made by INCO Company so that the oxygen content became 0.44, 0.60 and 1.55 wt% and then dropped in cold water in order to produce shots. These were sifted separately and those of -14 mesh were gathered. They were acid leached sufficiently and the relationship between the chemical dissolution speed and the dependency on the oxygen content was investigated. 0.6 L of copper anode solution was put in a 1 L reactor and reacted at a solution temperature of 90°C with vigorous agitation (1,000 rpm) at an air flow of 7 L/min. The results obtained are given in Fig. 6. The acid leaching speed increased for the sample with oxygen content 1.55 % and for the samples with oxygen contents higher than other samples (0.60, 0.44 %). This was thought to be due to the fact that under vigorous agitation the granules collided with one another and the

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corrosion product (equivalent to the slime film in the case of electrolysis of crude copper) could not stay on the granule surface, as a result, the dissolution activity was not hindered.

4. Discussion

When the facts given in the previous section 3 are put together, it is easy to see where differences originate: the differences in which one claims that anode oxygen for the anode activity in copper electrolysis is effective and the other claims that it has a contrary effect. The decisive factor for the physical properties (thickness and porosity) of the slime layer which has a considerably bad effect on the dissolution activity of copper can be obtained from the composition and temperature of the solution, and, or, the load current density. However, it is thought to be appropriate that a more direct and important factor should be obtained from the condition of distribution of the impurities in crude copper.

As it was perceived in this study, anode oxygen is one of the dangerous impurities. As it has been reported already[2], about 3-5 % of the Cu_2O phase[g] which exists in the crude copper anode enters the slime at the time of anode dissolution. If the oxygen level in the original material is

---

g) Suppose the oxygen content be 1,000-3,000 ppm, if this whole amount is used to form a Cu_2O phase, the amount occupies 0.9-2.7 wt%.

increased gradually, the Cu_2O entering rate increases further. For instance, the result of calculation of incomings and outgoings of substances for the oxygen level of 7,200 ppm showed 8 % in one example. Thus Cu_2O has a great effect on the determination of physical properties of the slime layer as one of the principal components.

Secondly, let us study nickel as an anode impurity other than oxygen that effects the slime properties. The reason is that the crude copper sample used in this experiment had a characteristic of having about 4,600 ppm of Ni content. It has already been reported[9] that, in the case of anode copper with a normal composition, the rate of Ni entering the slime is 5 % at the highest as has been shown by experience at many electrolytic factories. In this case, much of anode Ni is metallic and consequently it goes through the process of $Ni^0 \rightarrow Ni^{2+} + 2_e^-$ ($E^0 = 0.25V$ vs. NHE) with electrolysis of copper, of oxidation and dissolution easily. On the other hand, in this experiment, the Ni content in the crude copper sample was already fairly high. Therefore it can be thought that if oxygen is added rapidly, the Cu_2O content increases accordingly and at the same time a part of added oxygen combines with Ni and a NiO phase is also formed. As the NiO phase[h] formed under high temperature is very stable, the rate of entering the slime may well increase. In fact, a very

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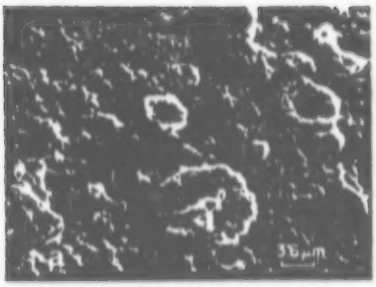
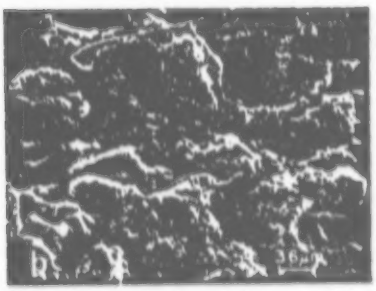
h) Refractory NiO



Anode slime G



Anode slime L

Fig. 7 SEM pictures showing two typical anode slimes formed from anodes G and L, respectively (2800x).

high rate of entering of about 40 % was obtained at 7,200 ppm as stated above. As can be seen from these examples, regardless of the distribution of impurities in crude copper, it can be thought that the total amount of Cu_2O + NiO in the slime increases greatly when a high oxygen/high Ni content is realized at the same time. If such crude copper is electrolyzed, it is estimated that the probability of the formation of passivation increases considerably.

Now two kinds of copper anodes were corroded for 24 hours under normal electrolysis conditions. Then the surface of the slime layer formed was studied by SEM observation.

Table 2 Anode composition and slime analyses.

[A] Anode composition (ppm).

Anode	O	Ni	Pb	As	Sb	Se	Ag	S	tp (min)
G	1800	2237	371	289	309	149	337	45	10
L	1700	4638	83	45	5	371	352	10	1

[B] XRD analysis of slimes formed.

Slimes	Major Phase	Minor Phase	Very Minor Phase
G	$PbSO_4$	Ag^0, Cu_2O, CuAgSe	$Cu_{2-x}Se$
L	Cu_2O, NiO	Cu^0, CuAgSe	$Cu_{2-x}Se$, NiOOH

The results are given in Fig. 7. The composition for both copper anodes is given in Table 2 [A]. It appears that sample G contains somewhat more impurities than sample L. On the other hand, the oxygen content was almost the same for both. The former has a characteristic of containing 2,237 ppm of Ni, half the amount of the latter. t_p was measured and the sensitivity for passivation of both samples was compared. Contrary to the expectations, the value of t_p of sample L was very small, 1 minute, compared with that of sample G, 10 minutes, which was considered to be more impure. As if supporting this result, it seems that the slime layer (Picture b) formed from the former is very thick and dense. The results of XRD analysis are given in Table 2 [B]. The main components of this very thick slime were NiO and Cu_2O phases. On the other hand, the main component of slime G (Picture a) was $PbSO_4$ and a Cu_2O phase was detected only as a secondary component. A very interesting point was that a NiO phase was not at all detected in this slime.

Furthermore the average particle diameter of Cu^0 p. 1293

powder which exists in the slime is usually smaller than 1 μ and so very fine. In the case of pure copper anode, this Cu^0 powder is formed by a monovalent dissolution and by a disproportionate reaction which follows[10]. In the case of crude copper, in essence, the Cu^0 powder may be formed by the same process as that for pure copper. One interesting fact is that the Cu^0 powder is often detected at the same time when Cu_2O exists in the slime as a main component as was observed in crude copper L. It is thought that this was due to another disproportionate process in which a part of Cu_2O phase went through the process expressed by $Cu_2O + H_2SO_4 \longrightarrow Cu^0 + CuSO_4 + H_2O$ inside the thick and dense slime with the addition to the part formed by the monovalent dissolution and disproportionate reaction. On the other hand, it is thought that the reason why the Cu^0 powder was not detected in slime G was that it became much easier for the dissolved oxygen and the free sulfuric acid from the solution at a distance from the copper anode to diffuse and enter deeply inside the slime layer due to the thinness and porosity of this layer. In this case, it is thought that it is more advantageous for the Cu_2O phase in the slime to reach a chemical dissolution through the process expressed by $Cu_2O + 2H_2SO_4 + 1/2O_2 \longrightarrow 2CuSO_4 + 2H_2O$ rather than through the disproportionate process and then to become Cu^0 powder.

5. Conclusion

From the results of the experiments given above, the

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following conclusions were reached.

(1) Anode oxygen, in essence, increases the dissolution activity of copper.

(2) However, at the same time the higher the level of oxygen the greater the formation of slime. This hinders further the diffusion of copper ions eluted from the anode surface. As a result, a nonconducting copper sulfate film is deposited on the anode surface and promotes passivation.

(3) Regardless of the distribution of impurities, when high level of oxygen and high level of Ni are realized at the same time, the probability of passivation greatly increases. This is due to not only the increase of the Cu_2O phase but also to the formation of inactive NiO phase in great quantity at the same time. As a result, the slime layer becomes thicker and denser.

(4) The stability of the Cu_2O phase in the slime increases as the thickness of the film increases. A part of the Cu_2O phase goes through a disproportionate process and forms Cu^0 powder. On the other hand, when the slime layer is thin and porous, the diffusion of existing oxygen and free sulfuric acid from the solution at a distance from the copper anode becomes comparatively easy. This starts the dissolution reaction with the Cu_2O phase in the slime and plays a role in decreasing the existing amount.

Finally, the authors would like to thank INCO Metals Company, Ltd. for giving them permission to publish this paper.

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Effect of Sulfuric Acid Concentration in Copper Electrolyte upon the Passivity of Copper Anodes*

– Anode passivation in copper refining (6th Report) –

by Shin-ichiro ABE[1] and Sakichi GOTO[2]

The previous observation that free H_2SO_4 concentration affects the passivation characteristics of copper anodes more than the concentrations of Cu^{2+} and Ni^{2+} was investigated in more detail.

It has been found that,

(1) Sulfuric acid concentration did not have a sufficiently strong effect upon such solution parameters as $\bar{D}_{Cu^{2+}}$, η and solubility of $CuSO_4$ to explain its strong passivating effect.

(2) A strong evidence has been obtained that the effect of acid is associated with a change in the slime structure, thus making it thicker and denser with increasing acid level in electrolyte.

A set of experiments of the permeability of water through a slurried bed made of each of the slime samples has shown that a layer of slimes formed through anodization at a higher acid level had lower permeability. Average particle size of the high-acid slimes appears to be finer. Some possible increase in the degree of amorphous fraction of this slime layer has also been discussed.

Slime fall also tends to increase with increasing acid concentration in electrolyte, but to such a small extent that it remains questionable whether this could be a major contributing factor to the dramatic increase in the tendency to passivate.

1. Foreword

The results presented in a previous report[1)] showed that the effect of the typical solutes ($CuSO_4$, $NiSO_4$ and H_2SO_4) of ordinary copper electrolyte upon the passivation times (tp) of crude copper anodes was great when varying the respective unit volumes of the various concentrations, stressing among others the case of sulfuric acid.

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* Received Sept. 30, 1980.

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Although the essential cause of passivation is the deposit of a copper sulfate salt film on the electrode surface[1)2)], the effect of the $CuSO_4$ solute upon tp is of a much smaller order and even smaller than the effect of $NiSO_4$.

In the present study we will examine the source of the specificity exercised by this sulfuric acid upon tp and establish therefore the following two hypotheses.

(1) Sulfuric acid acts specifically within a given concentration range with regard to the dispersion coefficient and solution viscosity which are thought to control the form of the copper ions transfered from the anodic surface to the distant solution, and more directly with regard to another parameter; viz., the degree of saturation solubility of the copper sulfate.

(2) Whether the amount of slime generated increases or whether there occur some qualitative changes in the slime structure compounds, ultimately the slime layer inhibits strongly the diffusion behavior of the copper ions.

We will present the results of our examinations pursued along these two hypothesis lines.

2. Tests

We first followed the changes observed in the copper ion diffusion coefficients ($\bar{D}_{Cu}^{2+}$), the viscosity (η) and the copper sulfate saturation solubility (C_s) when changing the concentration of the various solutes in copper electrolytic basis solutions (g/L: 40 Cu, 20 Ni, 200 H_2SO_4) and examined whether we could find the specificity exercised by sulfuric acid. Following this, we performed a comparative

examination to see whether we could find which difference in copper passivation behavior exists between the slime layer obtained by electrolyzing a certain type of crude copper and an artificial slime layer (Millipore filter paper: called hereafter MP paper). We also examined the kinds of changes taking place in the amount of slime produced and in the structural compounds according to the sulfuric acid concentrations.

As a rule, the testing temperature was 55°C.

3. Results of the tests

3.1 Measurements of the copper solution parameters

3.1.1 Measurement of the copper ions diffusion coefficient

The fact that the diffusion of the copper ions from the electrode surface is sometimes strongly inhibited through some action on the solution side is first conceived to be one of the factors accelerating the formation of a non-conductive copper sulfate film[a)] which is the direct cause of anodic passivation. So, following the convenient diffusion coefficient rapid measurement method of Tamamushi et al[3)], we examined the dependence of $\bar{D}_{Cu}{}^{2+}$ on the solute concentration. The diffusion membrane used for this diffusion cell is made of MP paper with a 1.2 μ pore size, about 120 μ thick. We first ascertained [b)] that it had enough resistance vs. a solution

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a) Identified as $CuSO_4 \cdot 5H_2O$ through X-ray diffraction.

b) After measuring $\bar{D}_{Cu}{}^{2+}$ 15 times in a row, we examined the cell constant. The results agreed with the initial values within a ± 3% range.

with a sulfuric acid concentration of 200 g/L. The test solution was prepared as follows. First suitable volumes (20 ± 10, ± 20 g/L Ni^{2+}) of only one solute in the copper solution are made to vary positively and negatively from the standard concentration point (for instance 20 g/L in the case of Ni^{2+}) and the other two solutes are maintained at their respective standard concentration points (Cu^{2+} : 40 g/L, H_2SO_4 : 200 g/L). The same procedure is followed when changing the concentrations of the other solutes. The prepared various test solutions are first packed (about 37 mL) in the lower chamber of the diffusion cell and then inserted carefully into the upper chamber fitted with a diffusion membrane. As at this time, some test solution goes through the diffusion membrane and permeates the upper chamber, it must be rinsed away swiftly 2 or 3 times with a small amount of pure water. Thereafter, pure water previously warmed to 55°C is used to fill the upper chamber gently to the same amount as that of the test solution. The moment at which this operation is completed was set to be the start of the experiment. The measurement time was always 3 hours.

The results are shown in Fig. 1. For convenience, one may refer in Fig. 2 to the tp changes of a crude copper sample measured[1)] p. 42 while varying in the same order the various solute concentrations. With $CuSO_4$ and $NiSO_4$, there was virtual agreement in copper ion diffusion behavior throughout the entire range of test concentrations. On the negative side of the standard point, $\bar{D}_{Cu}^{2+}$ showed a tendency toward a rapid surge. On the positive side to the contrary, the degree of $\bar{D}_{Cu}^{2+}$ decrease was weak. The reason seems to be that the total electrolyte concentration in this range was already rather high. Moreover, the diffusion index of the Ni^{2+} ions themselves in standard

copper electrolyte is 1.31×10^{-5} cm^2/s and only slightly lower than that of copper ions. With H_2SO_4, one has the impression that the diffusion power of the copper ions throughout the entire range of the changed concentration volumes (150-225 g/L)is more strongly inhibited. From this exclusive viewpoint, it is not desirable to raise too much the sulfuric acid concentration of industrial electrolyte.

In any case, it was completely impossible to note any sulfuric acid specificity reflected in the tp when comparing the two graphs in Figs. 1 and 2.

We computed the activation energy the copper ions diffusion from the results of sulfuric acid concentration dependence on the part of the series of $\bar{D}_{Cu}^{2+}$ values measured within the 45-65°C solution temperature range (Fig. 3). The values with regard to standard electrolyte are 10 kcal/mol, and much higher than the 4.6 kcal/mol value found by Awakura et al[4] for a 0.6 Cu + 0.6 H_2SO_4 (mol/L) solution.

3.1.2 Viscosity measurement

Thereafter we examined the effect of increased copper solution concentrations upon the viscosity. Since the copper ion concentration rose rapdily in the vicinity of the copper anode during the electrolytic progress, we performed the viscosity measurements on the basis of the following solution components. That is, we sought the η of a basic solution (g/L : 40 Cu + Me^{n+} + 200 H_2SO_4) with a first determined addition volume of particular dissimilar metallic ions Me^{n+} : Na^+, Ni^{2+} or Fe^{3+}). Thereafter, we changed variously [Me^{n+}] and sought the difference $\Delta\eta$ (rate of viscosity change) from the η values found when raising the copper ion concentration in the solution to 70 g/L. Fig. 4 shows the obtained results regarding the correlation of $\Delta\eta$ vs. [Me^{n+}]. When examining the state of $\Delta\eta$ changes in the case of

sulfuric acid, we performed tests while changing the amount of sulfuric acid added to the (40-70) Cu + 20 Ni (g/L) solution from 175 to 225 g/L.

These results showed that Δη increases in a rectilinear fashion together with $[Me^{n+}]$ and that the extent of change increases as the dissimilar metallic ion values rise. On the other hand, the extent of change per unit volume of sulfuric acid was smallest.

Fig. 5 shows the conditions in viscosity increase obtained when raising gradually to 40, 50, 60 and 70 g/L the copper ion concentration in copper solutions to which had been added respectively 20 g/L of metallic ions of these 3 types. The abscissa represents the ion products $[Cu^{2+}] \times [SO_4]^7$. In all cases the viscosity shows a tendency toward a rectilinear increase and the ion value also has a great effect.

3.1.3 Measurement of copper sulfate saturation solubility

We added to 200 g/L sulfuric acid aqueous solutions different volumes of the various dissimilar metallic ions, and allowed these solutions to be saturated with copper sulfate salts. The results are shown in Fig. 6. It is obvious that the extent of drop in saturation solubility when adding Ni^{2+}, Fe^{3+} ions which are higher in ion value, is much larger than that observed when adding Na^{+}. When examining the effect of the amount of sulfuric acid added upon saturation solubility, we added 20 g/L Ni^{2+} ions to the test solution. The results are shown in Fig. 7. The decrease rate of saturation solubility per unit volume of sulfuric acid addition is around -12 g Cu/mol H_2SO_4 in the vicinity of 200 g/L and about half as compared for instance to Ni^{2+} or Fe^{3+}. We see in Figs. 6 and 7, that the Cs - curves deviate from rectilinearity at the respective particular concentration points. The reason seems to

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be that in addition to the dissolution equilibrium reaction $CuSO_4(S) \rightleftarrows Cu^2 + SO_4^{2-}$ in the saturated solution system, there occurs also a formation of some equilibrated system[2].

3.2 Effect of sulfuric acid upon the slime structure

First electrolyzing for 24 h at a solution temperature of 50°C and 200 A/m² a small test piece (4 x 12 x 1 cm) cut out from INCO crude copper, we obtained the formation of a slime layer having a quasi-equilibrated membrane thickness. This anodic treatment was carried out in copper basic solutions[c] to which sulfuric acid had been added in the respective amounts of 100, 150, 175, 200 and 225 g/L. Thereafter, we removed gently the variously treated test pieces from the electrolytic cell without damaging the slime layers and transferred them to tp measurement cells[d]. The pieces were left there soaking for about 30 min and then measured for tp at 400 A/m². Consequently, if a meaningful difference is noted in the series of tp readings, it should be based mainly on the "acidity effect".

Fig. 8 shows the results (solid lines) regarding the correlativity of tp vs. $[H_2SO_4]$ obtained with regard to crude copper samples containing 3 types of oxygen values (450, 1,900 and 5,000 ppm). It is obvious from this that tp drops suddenly with an acid concentration above 150 g/L and that as we reported earlier[1)5)] there is more sensitivity with regard to passivation as the oxygen level in the anode is high.

By increasing the sulfuric acid concentration in the above tests, we raised, of course, the acidity of this electrolyte but we are

---

c) 40 g/L Cu + 20 g/L Ni.

d) 40 g/L Cu + 20 g/L Ni + 200 g/L H_2SO_4 (50°C).

also supposed to have increased the concentration of the total sulfuric acid ions. It is possible that there was some change in the slime structure because of the occurrence of a reaction such as "sulfation" produced between some slime compounds. So, in order to separate the "acidity effect" from such possibility, we performed the following tests. First, when carrying out the aforementioned anodic preliminary treatment, we took the 40 Cu + 20 Ni + 100 H_2SO_4 (g/L) composition test solution as standard. Thereafter, instead of adding sulfuric acid we added each time suitable quantities of sodium sulfate salt. "Suitable quantities" means quantities equivalent to sulfuric acid additions of precisely 150, 175, 200 and 225 g/L in ionic strength. However, when preparing an ionic strength equivalent to 225 g/L, there is a limit to the solubility of sodium sulfate. So we used instead the 125 H_2SO_4 + 144.8 Na_2SO_4 (g/L) combination.

The already referred to Fig. 8 shows also the series of tp measurements obtained (dotted line parts). It is shown that the tp value decreasing trend due to the increased sulfuric acid root* concentration is similar to the "acidity effect" result. However, we noted the occurence of a great difference between both in the tp values. These facts demonstrate that some structural change takes place in the slime because of the increased sulfuric acid addition volume, and that a stronger inhibition was brought about with regard to the diffusion of copper ions from the anodic surface. To ascertain this further, we p. 44 performed the following test. That is, when, for example, pressing as artificial membrane on pure copper anodic surfaces a substance such as MP paper whose geometrical structure is strictly regulated and whose initial structure is virtually unmodified by increased sulfuric acid

* translator's note : literal translation

additions (see 3.3.1), the passivation trend exhibited by this so-called "simulated aged anode" is estimated to be essentially the same with regard to the "acidity effect" and to the "total sulfuric acid ion effect", as long as the ionic strength is constant. Fig. 9 shows the results of passivation time measurements of the aforementioned synthetic anodes made along this line respectively in "acidity effect" baths and in "total sulfuric acid ion effect" baths. The graph shows that no significant passivation trend difference between both baths was obtained with regard to actual slime. At all points within the considered ion strength range the tp values correspond practically to one another. Judging from the results of Figs. 8 and 9, it seems that the reason for the specificity by which the acid sulfuric concentration affects the passivation of the crude copper anode lies in the fact that because of the sulfuric acid, the slime layer undergoes some change and becomes denser with the result that copper ion diffusion from the anodic surface is strongly hampered.

Regardless of the type of crude copper, the passivation curves of Fig. 8 begin to drop suddenly at a sulfuric acid concentration over 150 g/L. Such changes are also noticed with regard to artificial slime. This leads us to believe not so much that the sulfuric acid rendered the slime layer suddenly denser, but rather and more rationally that as the entire copper electrolyte concentration reached a certain critical level some qualitative change took place in the solution.

All sulfuric acid volumes in the slime samples obtained throughout the "acidity effect" tests were < 0.2 wt%.

3.3 Some views about the slime structure

By putting together the test results obtained so far, we see that the respective specificities of sulfuric acid upon the tp behavior are produced because some structural change is brought to the slime layer. It may be that such structural change took place only because the amount of slime generated increased and because the entire membrane became denser. The reason could also be that there was some interaction between some type of slime structural compounds and the sulfuric acid, and that the physical properties of the slime changed, finally inhibiting further the diffusion of copper ions. We will discuss hereunder the tests carried out along this line.

We electrolyzed crude copper samples (chemical composition shown in Table 1) for about 3 days in a copper solution whose sulfuric acid concentration was changed variously, found the amount of slime generation and simultaneously identified the phases of the main structural compounds of these slime samples by the X-ray diffraction and chemical analysis methods. From the results arranged in Fig. 10, we first see that the volume of slime formation tends to increase even if only a little as the amount of sulfuric acid becomes greater. Furthermore, the volumes of the two phases Cu_2O, NiO which are the main and accessory components in these slimes[e)] increase also somewhat. These results provide a qualitative explanation for the fact that the copper anode passivation trend increases certainly. Yet the question remains as to whether such amount of slime increase can

---

e) Other accessory components such as Cu^o and trace components such as CuAgSe, Ag^o, Cu_{2-x} are simultaneously detected.

really produce in the tp behavior the dramatic changes already referred to in Fig. 2.

So, we built the simple device shown in Fig. 11 and performed qualitative tests about the fineness of the components constituting the slime. Of course, one obtains simultaneously information about the level of amorphism presented by the entire slime. We washed thoroughly with water the slimes obtained by electrolysis at the respective sulfuric acid concentration levels of 150 and 200 g/L, injected this slurry in the present apparatus and allowed first through natural precipitation the formation of a 3.0 mm thick layer. MP papers of p. 45
various pore sizes were spread under this slurry layer. We obtained the amounts of pure water allowed to go through this double layer for a given time. Fig. 12 shows the results obtained with regard to the correlativity of the volumes of water passage vs. the series of pore sizes. For the sake of comparison, we performed similar tests, using copper powder (average particle size: 5-20 μ) obtained through pure copper electrolysis. Since copper powder is on the whole coarser than actual slime, the volume of water passing through this copper powder bed is judged to be fairly larger than that going through a slime bed. The results obtained corroborate these estimations (curve a). In this curve a the fact that the water passage reaches suddenly a ceiling when the pore size is 5 μ or more is noteworthy. The reason seems to be that when the copper powder begins to penetrate the pores, there is a conspicuous plugging effect. On the other hand, when we observe the overall behavior of passing water quantities vs. pore size changes (curves b and e) with regard to actual slime, we see that the slime produced through electrolysis at high sulfuric acid levels is denser.

The curve c of this slime gives a minimum at a pore size of about 0.6 μ. A possible explanation is that the average particle size of the slime particles plugging the MP paper pores is widely distributed in this vicinity. With slime produced through electrolysis from low sulfuric acid levels, the minimum point on this curve appears in the vicinity of a somewhat larger pore point (0.8 μ).

4. Conclusion

By coordinating the test results obtained in the present study, we may draw the following conclusions.

(1) The specific action of sulfuric acid upon the passivation tendency of crude copper anodes is a phenomenon which occurs because the generated slime layer is made thicker and denser. It is not because of any specific action exercised upon the characteristics of the copper electrolyte, viz., the copper ion diffusion coefficent, the viscosity of the solution or the saturation solubility of copper sulfate.

(2) One of the reasons for such structural changes in the slime is the increased slime production concomitant to the increase in sulfuric acid concentration. It also seems that some special slime structural compounds produce some reaction with the sulfuric acid and that the particles become finer. It is also possible that the characteristics of the whole slime layer come to present more amorphism and that even with a small volume, it contributed to clog the pores of the slime further. Additional research is to be done.

(3) Ni^{2+} which is a dissimilar metal always contained in variable quantities within actual copper electrolyte has the remarkable effect of accelerating the deposit of copper sulfate salts on the copper

anodic surface. From the viewpoint of passivation prevention management, more efforts have to be made to keep the level as low as possible.

(4) The level of sulfuric acid in the copper electrolyte should not exceed 200 g/L. If possible, it is preferable to keep it at 180 g/L.

We wish finally to thank the INCO Metals Co. for authorizing the publication of the present study.

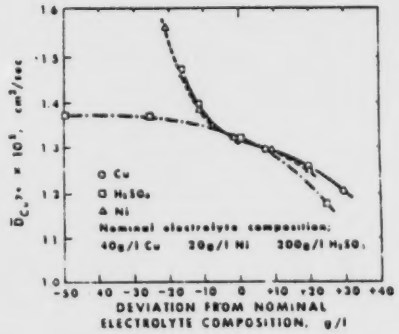

Fig. 1 Variation of diffusivity of Cu^{2+} ions with level of Cu, H_2SO_4 and Ni (55°C).

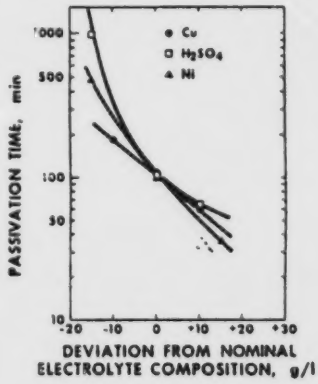

Fig. 2(*) Variation of passivation time with level of Cu, H_2SO_4 and Ni for anode A at 400 A/m² and 50°C. Nominal electrolyte composition is (in g/l): 40 Cu, 25 Ni, 200 H_2SO_4, 12 Na_2SO_4.

(*) Cited from reference (1).

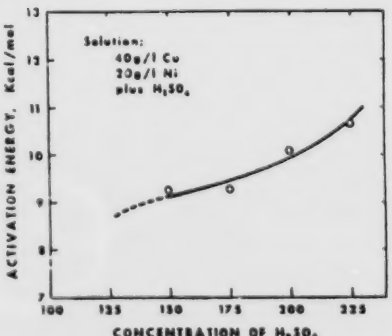

Fig. 3 Activation energy of the diffusion of Cu^{2+} ions in copper electrolyte.

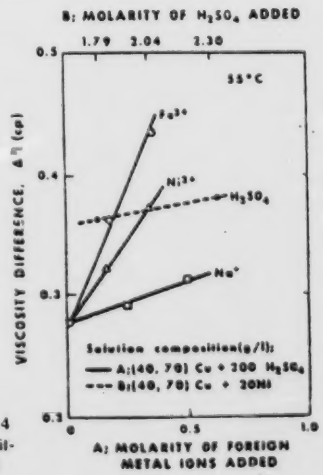

Fig. 4 Effect of foreign metal ions upon difference of viscosity values measured at two different Cu levels.

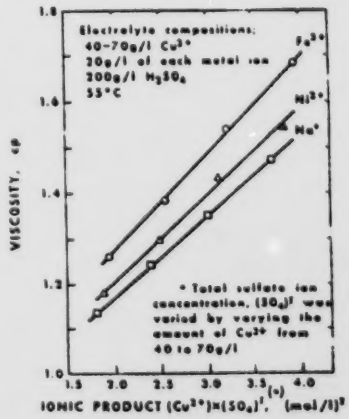

Fig. 5 Variation of viscosity with level of foreign metal ions in copper electrolyte.

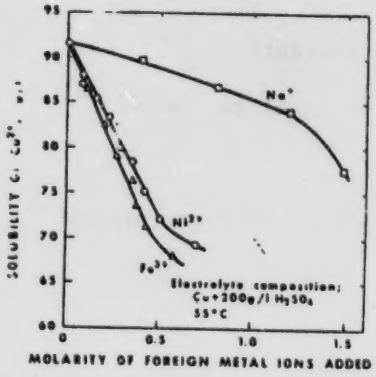

Fig. 6
Solubility of $CuSO_4$; effect of the presence of different foreign metal ions.

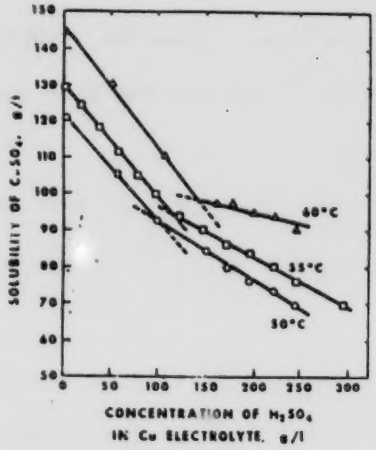

Fig. 7(*)
Solubility of $CuSO_4$ in copper electrolyte at different levels of H_2SO_4.
(*) Cited from reference (2).

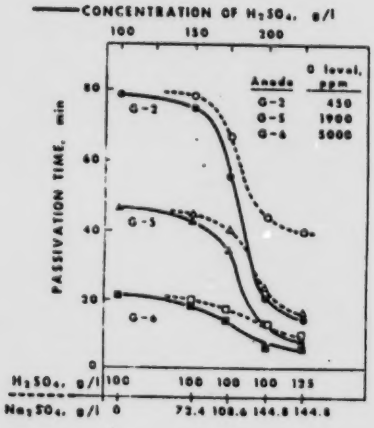

Fig. 8
Effect of H_2SO_4 concentration in copper electrolyte upon passivity of copper anodes (50°C).

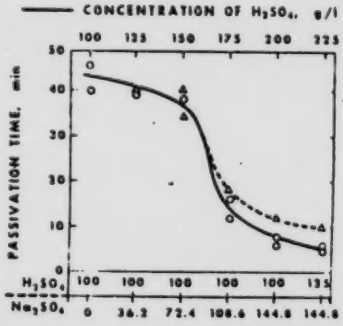

Fig. 9
A mutual separation of acidity and ionic strength effects using a simulated aged anode of copper (50°).

Table 1 Chemical composition of copper anode used in this study.
– all in ppm.

Element	O	Ni	Pb	As	Sb	Se
Level	7300	3239	27	45	1.8	409
	Te	S	Fe	Bi	Sn	Ag
	50	113	17	18	<0.5	520

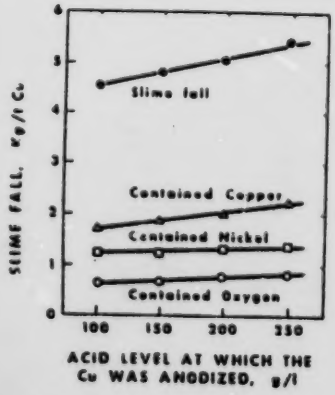

Fig. 10 Variation of slime fall of copper anode (*) with level of H_2SO_4 in copper electrolyte (50°).
(*) See table 1 for its composition.

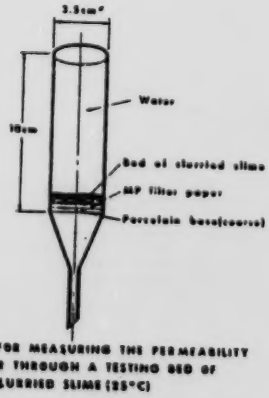

Fig. 11 Apparatus used for the experiments in Figure 12.

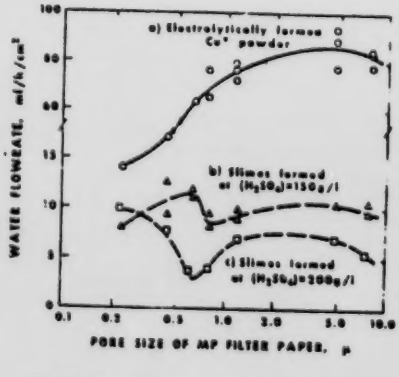
a) Electrolytically formed Cu+ powder
b) Slimes formed at (H2SO4)=150g/l
c) Slimes formed at (H2SO4)=200g/l
WATER FLOWRATE, ml/h/cm²
PORE SIZE OF MP FILTER PAPER, μ

Fig. 12 Permeability of water through the testing slurry bed as a function of pore size of millipore filter paper (25°C).

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Effect of Electrolyte Temperature upon Passivity of Copper Anodes*

- Anode passivation in copper refining (7th Report) -

Shin-ichiro ABE[1] and Sakichi GOTO[2]

The known effect of increasing electrolyte temperature in preventing anode passivation in copper refining was extensively reviewed.

It has been found that a layer of anode slimes formed at a higher electrolyte temperature tends to become more porous with the simultaneous decrease in slime fall. While this increased permeability allows the diffusing ability of Cu^{2} ions away from the surface of a corroding anode to increase, a gravitational flow of the electrolyte also becomes more pronounced within the slime layer. That is, more concentrated copper electrolyte at the anode surface streams downwards through the micro pores and cracks, and this type of mass transport removes excessive Cu^{2+} ions far more efficiently.

A thorough investigation of electrolyte properties such as diffusion coefficient of Cu^{2+} ions, viscosity, solubility of copper sulfate and vapor pressure, etc. measured using copper electrolyte of a nominal composition over the temperature range 45-65°C, proves the fact that the gravitational flow is a predominant factor contributing to the decreased tendency to passivate at a higher temperature.

That anode passivation occurs more readily at a lower level of anode height is also explainable by this claim.

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* Received September 30, 1980.

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1. Introduction

In the preceding reports of this series of studies on anode passivation in copper refining, despite the practice in copper refineries of operating at a bath temperature of about 60°C, we have carried out our experiments at a temperature of 50°C (occasionally at 55°C)[1-7]. This departure is based on our finding that passivation time (t_p), which was used as one of the basic parameters in comparing passivity among various crude-copper anodes, could be determined with fairly good reproducibility at this lower temperature. Nonetheless, it has been our ultimate objective to

study the matter at temperatures conforming to the actual operating conditions.

It is frequently observed that a rise in electrolyte temperature in copper electrolysis cells moderates anode passivation. This effect has in general been attributed mainly to factors originating in the electrolyte such as increases in the saturation solubility of copper sulfate and the diffusion ability of copper ions (Cu^{2+}) and a decrease in the viscosity of the electrolyte.

In the studies of this series, these temperature-dependent aspects of various properties of copper solution were systematically examined with standard industrial electrolytes. The results of these examinations, however, suggested that the marked increase in $\underline{t}_{\underline{p}}$ at elevated electrolyte temperatures can not be fully accounted for by changes in the factors originating in the electrolyte alone. Not until one more effect resulting from the temperature increase, i.e., a decrease in the amount of slimes formed and a simultaneous increase in the porosity of the slimes had been taken into consideration, had a clear explanation become possible. The results of this aspect are described in this report.

2. Application of Mass Transport Concept to Anode Systems

The real cause of anode passivation in copper refining is the covering of anode surface by electricity-nonconducting

films of copper sulfate ($CuSO_4.5H_2O$).[1,4,5] This covering occurs when the concentration of copper sulfate surrounding the anode has reached a point of saturation.

Since copper ions that are continuously dissolved and supplied from the surface of the anode move with a limited speed, the concentration of copper ions near the anode ($\underline{C}_o$) is always maintained at a higher level than that away from the anode ($\underline{C}_b$). The relation between this concentration difference ($\underline{C}_o - \underline{C}_b$) and load current density ($\underline{j}$) is expressed by the following equation:

$$j = nFK(C_o - C_b) \quad \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

$\underline{K}$: mass transport coefficient (cm/s)

$\underline{F}$: Faraday constant

Under the condition where $\underline{C}_o$ exceeds the saturation solubility of copper sulfate ($\underline{C}_s$), a relation expressed by the following equation exists:

$$C_o = \frac{j}{nFK} + C_b > C_s \quad \cdots\cdots\cdots\cdots\cdots\cdots (2)$$

Such a condition can be created, when all other electrolysis conditions remain constant, by raising the load current density beyond a certain level.

On the other hand, increasing $\underline{C}_s$ by any means is effective in preventing copper sulfate from precipitating out. This effect is realized easily by raising the electrolysis bath temperature.

According to equation (2), a close relationship exists between $\underline{K}$ and $\underline{C_s}$, but this relationship has been poorly studied. The concentration gradient of copper ions near a pure-copper anode on which virtually no layer of slimes forms will in general take a form like the one shown on the left-hand side of Figure 1. In this case $\underline{K}$ is described as

$$K = \bar{D}/\delta_N \quad \cdots\cdots (3)$$

where $\underline{\bar{D}}$ is the diffusion coefficient of copper ions and $\underline{\delta_N}$ the thickness of Nernst diffusion layers, the value being about 0.3 cm in an ordinary electrolysis system[1]. On the other hand, in the neighborhood of a crude-copper anode, on the surface of which a layer of slimes always exists, the concentration gradient shapes as the form displayed on the right-hand side of Fig. 1. In this case, equation (3) must be corrected for two main parameters that characterize the physical properties of the slimes, i.e., thickness ($\underline{\delta_s}$) and porosity ($0<\alpha<1$), as follows:

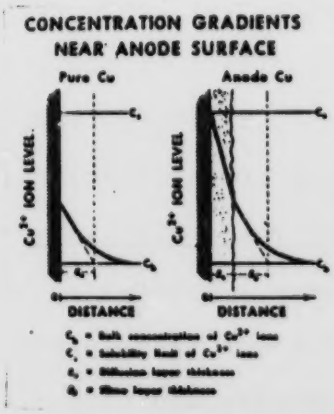

Fig. 1 (•) Schematic representation of the concentration gradients at refined and unrefined Cu anode surfaces at the same current density.
(•) Cited from reference (1).

$$K = \frac{\bar{D}}{\delta_N + \frac{\delta_s}{\alpha}} \quad \cdots\cdots (4)$$

Although unavoidably restrained by the presence of slime layers on anode surface, the movement of copper ions in a crude-copper anode system is increased within allowable limits with decreasing thickness and with increasing porosity of the slime layers. (p.114)

3. Experiments and Results

In examining the moderating effect of electrolyte temperature increase on the passivity of copper anodes, the following experiments were carried out to separate factors originating in the electrolytes from those coming from the slimes.

3.1 Electrolyte temperature-dependent changes in copper electrolyte properties

The effects of electrolyte temperature on the diffusion coefficient of copper ions, viscosity of electrolytes, saturation solubility of copper sulfate, and vapor pressure[a] of water in copper electrolytes were systematically examined with a standard copper electrolyte solution[b].

a) Density and viscosity

Figure 2 illustrates the results of an experiment in which the effect of electrolyte temperature varying from 25 to 65° C on density and viscosity was investigated. Both

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a) As a relative index giving the mole number of effective water.

b) Composition of the solution was 40 g/l Cu + 20 g/l Ni + 200 g/l H_2SO_4.

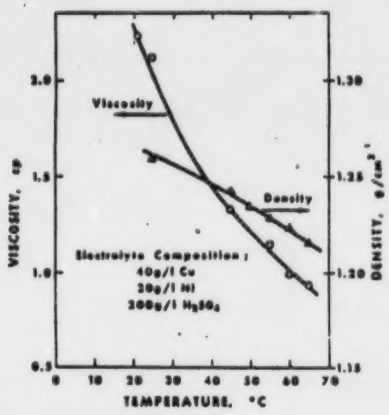

Fig. 2
Density and viscosity versus temperature.

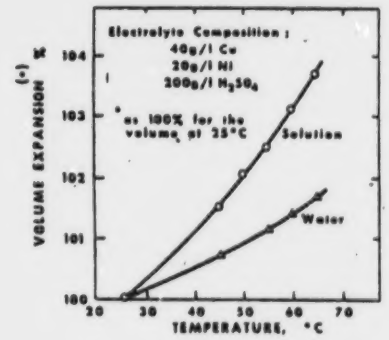

Fig. 3
Thermal expansion of electrolyte volume.

density and viscosity were markedly affected by temperature. Changes in the volume expansion of the experimental electrolyte, which was calculated from the density values obtained, are presented in Figure 3 in percentage, the value at 25° C being 100. Included in Fig. 3 are also changes in the volume expansion of pure water. When these changes are compared between copper solution and water, the rate of volume expansion changes for the copper solution was about twice that for the pure water within the temperature range of the experiment. In the copper sulfate solution, which is a concentrated solution, thermal intermolecular movements of solute molecules are likely to have been taking place more vigorously than those in the pure water.

In addition to the temperature-dependent changes in the viscosity of the standard copper solution (see Fig. 2), those of the same solution in which copper concentration was

raised to 70 g/l were also examined and the differences in viscosity between the two copper concentrations at each temperature (viscosity change rate: $\Delta\eta^{7)}$) are shown as a function of temperature in Figure 4. It is clear from this figure that $\Delta\eta$ tends to decrease slowly with rising temperature, indicating that the effect of electrolyte temperature on viscosity is greater in a concentrated than in a dilute electrolyte solution.

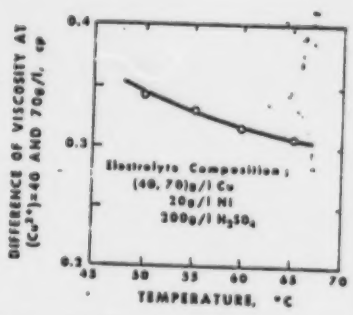

Fig. 4 Difference of viscosity at two different levels of Cu^{2+} concentration in copper electrolyte.

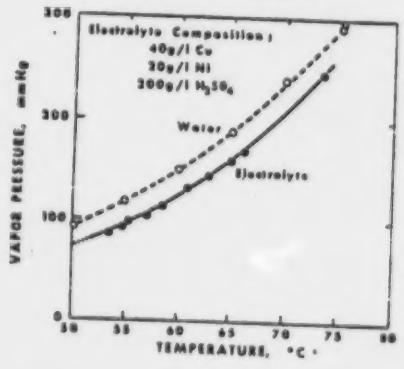

Fig. 5 Vapor pressure versus temperature.

b) Vapor pressure

Water vapor pressure was measured in pure water and in the standard copper electrolyte solution between 50 and 75° C (Figure 5). When one applies the theory of vapor pressure depression, which was obtained by Raoult's law as expressed below

$$\frac{P_0 - P}{P_0} = \frac{(1-\gamma)N + n}{n+N} \quad \cdots\cdots (5)$$

(P_0, P: Vapor pressures of pure water and solution; n, N: mole numbers of solute and solvent in the solution; γ: activity constant of water)

the value of γ is seen to increase gradually with increasing electrolyte temperature. When calculated from equation (5) on the basis of the density data of this electrolyte solution in Fig. 2, γ values at 50 and 60° C become 0.902 and 0.966, respectively. Judging from the γ value of 0.9 (H_2SO_4 = 2.24 mole) obtained by Robinson and Stokes[8] for a H_2O--H_2SO_4 system (at 25° C), these values appear reasonable.

c) Diffusion coefficient of copper ions

The diffusion coefficient of copper ions in the standard copper electrolyte solution was measured between 45 and 65° C in a diffusion cell system improved by Tamamushi et al.[7] In this experiment Millipore filter paper (pore diameter 1.2 μ x thickness about 120 μ; abbreviated hereafter as MP paper) served as diffusion membrane and it was confirmed before the experiment that the material of this filter paper had been hardly attacked by the acid in the electrolyte at temperature up to 65° C[c]. Values of $\bar{D}_{Cu^{2+}}$ that were obtained for a measurement period of 3 hours are shown as a function of electrolyte temperature in Figure 6. When the temperature rose from 50 to 60° C, the value of $\bar{D}_{Cu^{2+}}$ increased about 17%. (p.115)

d) Saturation solubility of copper sulfate

Copper sulfate (reagent grade) was added to a basic solution consisting of 20 g/l Ni and 200 g/l H_2SO_4 to prepare saturated solutions at 50, 55 and 60° C. According to an earlier report of this series[4], the concentration of free

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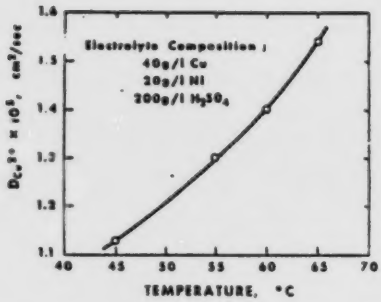
c) In a series of determinations for $\bar{D}$, cell constant values were the same within ± 3% before and after the determinations



← Fig. 6
Effect of temperature upon diffusivity of Cu^{2+} Ions in copper electrolyte.

Table 2 Chemical composition of INCO anode used in the present study.

Element	O	Ni	Pb	As	Sb	Se	Te	S	Fe	Bi	Sn	Au	Ag
Level (ppm)	2000	3750	54	45	<3	380	66	10	3	18	12	8	395

Table 1 Solubility of $CuSO_4$ at two different H_2SO_4 levels in copper electrolyte.

Temperature (°C)	Solubility, g/l, at 200 g/l H_2SO_4	Solubility, g/l, at 100 g/l H_2SO_4
50	77	92
55	83	98
60	95	111

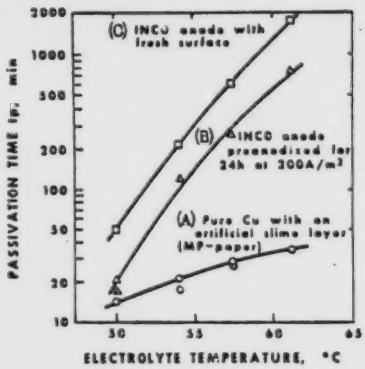

(C) INCO anode with fresh surface
(B) INCO anode preanodized for 24h at 300A/m²
(A) Pure Cu with an artificial slime layer (MP-paper)
PASSIVATION TIME (p), min
ELECTROLYTE TEMPERATURE, °C

Fig. 7 →
Effect of electrolyte temperature upon passivity of copper anodes with various surface conditions.

sulfuric acid near copper anodes at the time of equilibrium was reduced to about one half of that (200 g/l) away from the anodes. Hence another basic solution in which H_2SO_4 concentration was halved (to 100 g/l) was also prepared and used for the determination of saturation solubility. These results, which are summarized in Table 1, show that as temperature rose from 50 to 60° C, the value of C_s increased from 92 to 111 g/l, the increase being about 21%.

3.2 Electrolyte temperature dependence of passivation time

Meeting our expectation, the results that have hitherto been mentioned in this report on the relations of electrolyte temperature to the various properties of the copper electrolyte solution have all explained how the passivity of the copper anodes was reduced by elevated electrolyte temperature. These explanations, however, are merely qualitative. Hence

whether the amount of changes in some electrolyte parameters in a given temperature range, once known, will lead to a quantitative prediction of $\underline{t}_p$ changes can not be said with ease because of the structural complexity of slime layers themselves. Even if such a prediction is possible, this is based on the assumption that the structure of the slime layers is not influenced at all by electrolyte temperature.

In order to examine the effect of factors originating in the electrolyte on the amount of changes in $\underline{t}_p$ separately from those coming from the slimes, it is advantageous to use MP paper as an artificial slime membrane. This is due not only to the rigidity with which the geometric structure of MP paper materials is controlled but also to the fact that the structure of the slime layers is not at all affected by changes in electrolyte temperature (see section 3.1, paragraph c). Accordingly, when this artificial slime membrane is firmly fixed onto the surface of a pure-copper anode to prepare a "simulated aged anode", the results of the effect of electrolyte temperature on $\underline{t}_p$ obtained with such simulated aged anodes should theoretically reflect the amounts of changes in all electrolyte-side factors in a comprehensive manner. If comparisons of these results with those obtained with slime layers that were formed in an actual electrolysis operation yield any significant difference(s), this acts as a proof that the results in the latter case also included an influence

from the slime layers.

Thus the exposed surface (2.5 x 3.0 cm) of a small piece from a rectangular parallelopiped of pure copper. was buried in epoxy resin was polished with emery paper No. 600. MP paper[d)] was firmly fixed onto this polished surface to prepare an anode system which was used to examine the relationship between electrolyte temperature and $\underline{t}_p$. The results obtained at a current density of 400 A/m^2 and electrolyte temperatures of 50, 54, 57.5 and 62.5^o C are shown as curve A in Figure 7. Then a test piece (4 x 12 x 1 cm) of INCO crude-copper anode having a chemical composition shown in Table 2 was preanodized for 24 hours in the standard copper electrolyte solution at a current density of 200 A/m^2 to form a slime layer of semi-equilibrated thickness and a similar experiment was carried out (curve B). When curves A and B are compared, for the artificial slime layer the value of $\underline{t}_p$ increased about two times when electrolyte temperature rose from 50 to 60^o C, whereas for the slime layer formed under the real operating conditions this increase was 25-fold, supporting the notion that contribution from the slime layers was remarkable. Included in Fig. 7 as curve C were the results of $\underline{t}_p$ determination obtained with a piece of the same INCo crude-copper preparation, but with fresh surface, at a current density of 400 A/m^2.

In order to confirm the observed slime layer effect,

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c) pore diameter 1.2 μ x thickness about 120 μ.

we carried out the following experiment: a test piece of the same INCO crude-copper anode as was used in the experiments described above was subjected to preanodization for 24 hours at 200 A/m^2 and at 50, 55 or 60° C and each preanodized piece was transferred into a t_p-measuring cell (standard copper electrolyte solution at a temperature of 50° C) carefully without breaking any formed slime layer. After the piece was allowed to stand still in the cell for about one hour, the value of t_p was measured at a current density of 400 A/m^2. A similar experiment was carried out with another INCO crude-copper preparation (O = 5,000 ppm) and the results from these experiments are summarized together in Table 2 (Should read Table 3-- Translator's note). It is clear from this table that the effect of electrolyte temperature on the structure of slime layers and in turn on t_p is fairly large. (p.116)

Table 3 Effect of electrolyte temperature upon passivity of copper anode.

Anode	Passivation time (min) measured at 400 A/m^2 and at 50°C for anode preanodized(**) at the following different temperatures: 50°C	55°C	60°C
INCO anode	15	159	223
Anode G6(*)	7	13	35

(*) Another batch of INCO anode containing 5,000 ppm oxygen (reference 6).
(**) For 24h at a C.D. of 200 A/m^2 in the nominal copper electrolyte.

3.3 A few additional experiments on changes in the structure of slime layers

Based on the experimental findings that have been described in the preceding section of this report, we further studied the effects of electrolyte temperature on the amount of slime formation and on the distribution of slime components.

A large test piece (12 x 17 x 3 cm) of the aforementioned INCO crude-copper preparation was subjected to electrolysis in a 20-liter cell for 7 to 8 days at a current density of 200 A/cm^2 [e] and slimes formed were washed with water, dried, and subjected to phase identification by both chemical and X-ray diffraction analyses. The results of these analyses on slimes forming at 50, 57.5 and 62.5° C are presented in Tables 4 and 5. As can be seen from the results of the chemical

Table 4 Analyses of anode slimes formed at different electrolyte temperatures.

Temperature °C	Slime fall (kg/t Cu)	Amount of element disposed (kg/t Cu)							Permeability of water through a bed of slurried slime (ml/cm², h)
		Cu	Ni	Pb	As	Se	Ag	O	
50.0	2.8	1.23	0.12	0.05	0.015	0.37	0.43	0.22	9.5
57.5	2.4	1.0	0.10	0.04	0.013	0.34	0.42	0.15	13.4
62.5	2.2	0.85	0.07	0.03	0.010	0.37	0.44	0.12	19.7

Table 5 Phase identification of compounds present in anode slimes formed at different electrolyte temperatures.

Temperature	Phase identification by XRD; Major phase	Next major phase	Minor phase	Very minor phase
50°C	Cu_2O	Cu Ag Se, Cu_{2-x} Se	NiO, Cu^o, $PbSO_4$	Ag^o, UI (•)
62.5°C	Cu-Ag Se, Cu_{2-x} Se	Cu_2O	NiO, Ag^o	$PbSO_4$, UI (•)

(•) unidentified phase

analysis in Table 4, the amount of slime formation tended to decrease gradually with increasing electrolyte temperature. This decrease is considered to have resulted from a reduction

e) The electrolyte (standard copper electrolyte solution) was gently circulated through a bypass that was installed outside the cell to make the composition of the electrolyte uniform. The corroded surface of the test anodes after electrolysis appeared nothing unusual.

in the amounts of copper, nickel, and lead compounds in the slimes. According to the results of the phase identification analysis in Table 4, the main components of the slimes that formed at 50° C was Cu_2O, followed by CuAgSe and $Cu_{2-x}Se$. The minor components of the slimes included NiO, Cu^0, and $PbSO_4$. The Ag^0 phase was present only in an extremely minute quantity. On the other hand, present in slimes that formed at 62.5° C were all of those various phases that have been described above with the exception of Cu^0 which was absent. It appears in general that at the higher electrolyte temperatures, of the various slime components, copper compounds were affected stronger by acid extraction than others. Although nickel compounds were reduced to the same extent as the copper compounds, they remained as a secondary component.

Then the effect of electrolyte temperature on the porosity of slime layers was quantitatively assessed as follows: a bed of slurried slimes was allowed to develop to a thickness of 3 mm on its own weight in the aforementioned improved cell system[7] and the flow of pure water passing through a double layer, which was formed by the slurried slime bed and a sheet of MP paper that had been laid below the slime bed, was measured. The measurement was repeated three times for each slime sample to obtain averages which are shown in Table 3 (Should read Table 4--Translator's note). It is seen from this table that the volume of water passage tended to increase

with increasing electrolyte temperature at which the slimes formed. It should be noted here that the results on water passage provide information of events after the slime layers had completely been destroyed. Nevertheless, regardless of whatever the three-dimensional structure of the slime layers before destruction might have been, there is no doubt that slime materials after slurrying remained to form the basic structure of the slime layers.

4. Discussion

Slime layers that cover the surface of a crude-copper electrode (anode) in copper refining form a third system, which is sandwiched between first and second systems, i.e., the anode and the electrolyte. Copper ions that are continuously being supplied during electrolysis from the surface of the anode can not be transported into the electrolyte via any route other than this third system. Regardless of no matter how high the dissolution activity of the anode itself may be and how high the electrolyte may have a capacity to dissolve copper sulfate, if this transport of copper ions does not take place fast enough, $\underline{C_0}$ reaches $\underline{C_s}$ and the development of anode passivation merely becomes a matter of time.

The transport of copper ions from the surface of the anode takes place in four different types: 1) diffusion, 2) viscous liquid flow, 3) natural convection, and 4) transport

of charged particles along the flow of an electric current. When mass transport through pores of slimes that are formed under actual electrolysis-operating conditions comes into question, types 1) and 4) become important. Type 2) becomes important when these pores are oriented in an inclined rather than in a horizontal direction, since if all pores are assumed to be oriented in a regular manner in a horizontal direction extending to the electrolyte side, it is possible that a viscous liquid flow inside each pore tube lessens to such an extent as to become negligible. Inside actual slime pores, however, pore tubes are likely to be crossing each other and extend irregularly in all directions within a slime layer. According to the theory of probability, the state of such irregular distribution of numerous pores in all directions is expressed as "one-third of a total number of pores are oriented (p.117) in an inclined other than a horizontal direction". Under this condition the contribution of type 2) mass transport can no longer be ignored. Needless to say, since copper solution near anode surface is always maintained at a higher concentration than solution away from the anode, viscous flows under gravity which are propelled by this concentration difference in copper solution, are expected to occur by passing through these pore tubes with an inclined orientation.

In the artificial slime layer, when electrolyte temperature rose from 50 to 60° C, the value of $\underline{t}_p$ increased about

two-fold. In this layer of MP paper having a porosity of 80%, pores extend regularly in a horizontal direction without crossing each other. The transport of copper ions through these horizontally oriented pores takes place by means of types 1) and 4), and type 2) is not expected to occur. On the other hand, in the slime layers that formed under the actual operating conditions, despite the fact that the thickness of the slime layer was estimated at 200 μ--about twice that of MP paper, artificial slime layer, the corresponding increase in $\underline{t}_p$ was about 25-fold and the $\underline{t}_p$ values at each temperature were also fairly high (see Fig. 7). Even if the average diameter of the pores formed under the actual operating conditions is assumed to have been much larger than 1.2 μ (of MP paper) and when effective total cross-sectional area (i.e. porosity), which allows copper ions to diffuse from anode surface, was in the neighborhood of 80%, the same as that of MP paper, the amount of copper ions that was removed through diffusion should not have yielded such a large difference. Also, when the porosity is assumed to have been slightly larger than 80%, it is difficult to imagine that such a small increase would have contributed substantially to the 25-fold increase in $\underline{t}_p$. All of these arguments point to a need for consideration of a type of mass transport in which efficient removal of copper ions is effected by the gravitational viscous flow of the electrolyte through the pores with an inclined orientation

According to Stokes' law, the moving ability of a liquid under gravity is proportional to the fourth power of the diameter of small tubes through which the liquid passes. In the present study, the porosity of slime layers has been found to increase with increasing electrolyte temperature. This increase is likely to have acted as promoting the moving capacity of the electrolyte rather than as proportionally increasing the amount of copper ions that were diffused.

The fact that passivation developing in electrolyte cells is most frequently observed at the lower part of crude-copper anodes seems to support the above notion. Also, this gravitational viscous flow is helping to replace, continuously though slowly, concentrated electrolyte remaining inside the slime layers with diluted electrolyte moving into the layers from surrounding areas and such replacement will be effective in preventing the concentration of copper ions on an anode--slime interface from increasing to abnormally high levels.

5. Conclusion

The cause of the reducing effect of increased electrolyte temperature on the passivity of copper anodes was examined from two sides--electrolyte and slime-- separately. As had been expected, the relations of a few basic parameters of a standard copper electrolyte solution (diffusion coefficient, viscosity, saturation solubility of copper sulfate, and mole number of effective water) to electrolyte temperature were

all found to be useful in reducing anode passivation.

On the other hand, the thickness of slime layers decreased and their porosity increased with increasing electrolyte temperature. These changes would result in accelerating the diffusing ability of copper ions from the surface of the anode. There is also a good possibility that concentrated electrolyte forming at the anode surface underwent a gravitational flow through the inclined rather than through the horizontally oriented pore tubes existing in numerous quantities in the slime layers, resulting in transport of excessive copper ions off the anode.

We thank INCO Metals Company, Ltd., Canada, for having allowed us to publish this report.

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Effect of Electrolyte Temperature upon Passivity of Copper Anodes

—— Anode passivation in copper refining (7th Report) ——

by Shin-ichiro ABE[1] and Sakichi GOTO[2].

The known effect of increasing electrolyte temperature in preventing anode passivation in copper refining was extensively reviewed.

It has been found that a layer of anode slimes formed at a higher electrolyte temperature tends to become more porous with the simultaneous decrease in slime fall. While this increased permeability allows the diffusing ability of Cu^{2} ions away from the surface of a corroding anode to increase, a gravitational flow of the electrolyte also becomes more pronounced within the slime layer. That is, a more concentrated copper electrolyte at the anode surface streams downwards through the micro pores and cracks, and this type of mass transport removes excessive Cu^{2+} ions far more efficiently.

A thorough investigation of electrolyte properties such as diffusion coefficient of Cu^{2+} ions, viscosity, solubility of copper sulfate and vapor pressure etc. measured using copper electrolyte of a nominal composition over the temperature range 45 – 65°C, proves the fact that the gravitational flow is a predominant factor contributing to the decreased tendency to passivate at a higher temperature.

That anode passivation occurs more readily at a lower level of anode height is also explainable by this claim.

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EFFECT OF ANODE OXYGEN LEVEL UPON DISSOLUTION CHARACTERISTICS OF COPPER ANODE*

-- ANODE PASSIVATION IN COPPER REFINING (8TH REPORT) --

Shin'ichirō ABE[1] and Sakichi GOTŌ[2]

A set of Cu-O binary alloys with their oxygen contents being adjusted in the range 100 – 8 900 ppm was prepared, and anodic dissolution experiments were carried out at 55°C to determine the effect of anode oxygen level upon dissolution characteristics in a copper electrorefining electrolyte.

It has been found that the dissolution behavior of the Cu-O anodes is greatly affected depending upon type of the microstructure. That is, % anode sludge formed, typically consisted of $Cu^0 + Cu_2O$, increases with increasing oxygen content in the hypoeutectic region until a maximum is reached at the eutectic point. This then is sharply decreased, followed by the gradual increase in the hypereutectic region.

An evidence was also obtained by means of electrochemical and X-ray diffraction techniques that a Cu_2O phase present in the matrix of copper anode is partially converted to a CuO phase as a result of annealing/slow cooling process employed to this anode, and also that such heat treatment brings about a drastic change in the dissolution behavior over the entire range of oxygen level studied.

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1. INTRODUCTION

In the previous report[1] when discussing the monovalent dissolution of the copper anode and the disproportionate reaction that follows it, a quantity called the b-value was introduced as the parameter that controls this electrode process. Furthermore, it was found that this quantity reacts with sensitivity to changes in the structure,

* Received on December 6, 1982

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temperature and agitation of the copper electrolyte. On the basis of these results from research into what is called external factors, this investigation was carried out to determine what effects are really caused by external factors such as anode oxygen, for example, on the b-value. This was done for two reasons, firstly, because the anode oxygen, in essence, plays the role of raising the dissolution activity of the copper anode[2], and, secondly, because in the plant the dissolution activity is greatly increased when an appropriate heat treatment is applied to the copper, and this seems to have some relationship to the occurrence of the phase change, represented by $Cu_2O \rightarrow CuO + Cu^o$, within the copper anode structure caused by the heat treatment[3].

In this article, using a set of Cu-O binary alloy samples having a simple composition prepared with a wide range of oxygen content as the anode, their dissolution behaviour was pursued as a function of oxygen content. Furthermore, as the need arose, the dissolution behaviour of a specific crude copper was also examined and was compared to that of the Cu-O anodes just mentioned.

2. EXPERIMENTAL METHOD

2.1 Sample Preparation

First reduced copper of high purity was prepared by electrorefining at the laboratory scale. This was then melted in an alumina crucible, and its oxygen concentration was adjusted in the range of 100 - 8,800 ppm by the addition

of an appropriate amount of Cu_2O powder (reagent grade). After this molten copper was solidified by being allowed to cool in a graphite mold, it was equally divided into two, and one portion was heat treated in an argon gas current, while the other portion was left untreated. The heat treatment was carried out by first maintaining the temperature at 1050°C for about 6 hours, gradually cooling to 150°C at an average rate of 15°C/hr, and then being allowed to cool down completely.

2.2 Dissolution Experiment

The surface of each anode sample was first prepared to the size of 9x5x1.5 cm, it was then polished to a No. 600 emery paper, and immediately after it was washed with water and the grease removed, the dissolution experiment was carried out. A 3 L capacity electrolytic cell was used, and within it were placed a pair of stainless steel cathodes in a cathode box with a test anode in the middle. Electrolysis was carried out while the anodes were entirely submerged in the electrolyte by having a titanium bar, which had been wrapped with insulation tape, screwed in the upper edge of each anode. The reason for this has already been explained[1]. The condition of electrolysis was as follows: electric current density 200 A/m^2; temperature of the solution 55°C; and the duration of electrolysis 40 - 48 hours.

At the end of each experiment, all of the anode sludge formed was retrieved, and immediately washed with

water and then with methanol, and, immediately afterwards, vacuum dried in a desiccator. It was assumed that the sludge was mostly composed of copper powder Cu^0 and Cu_2O compounds, and therefore, the estimation of the amount of Cu_2O present was made using their oxygen analysis values.

2.3 Calculation of the b-Value

The b-value for the dissolution of pure copper anode can be obtained by the following Equation (1)[1].

$$\bullet\ Cu^0 \rightleftarrows Cu^+ \rightleftarrows Cu^{2+} \quad (a)$$

(partially)

$$\longrightarrow \frac{1}{2}Cu^0 + \frac{1}{2}Cu^{2+} \quad (b)$$

$$\Delta W = \frac{63.54 \times I_1 \times (100+b)}{2 \times 100}\ (g) \quad \cdots\cdots (1)$$

Where ΔW is the weight decrease of the copper anode due to the dissolution caused by the total amount of electricity I_1 (Faraday).

On the other hand, in regard to the Cu-O binary anode to which oxygen is added, some concurrent reactions represented by Equations (2) to (4) are considered to take place besides this main reaction represented by Equation (1).

- Cu_2O (anode) + $2H^+ \longrightarrow 2Cu^{2+} + H_2O + 2e^-$

  (electrochemical dissolution) ..... (2)
- In parallel with Reaction (2), a part of Cu_2O is mechanically liberated to become sludge.

  Cu_2O (anode) $\longrightarrow$ Cu_2O (sludge) ..... (3)
- Partial acid exosmosis of Cu_2O that was liberated into the sludge takes place.

  $Cu_2O + 4H^+ + 1/2O_2 \longrightarrow 2Cu^{2+} + 2H_2O$ ..... (4)

In this manner, the weight decrease of the anode obtained by the anodic dissolution of Cu-O binary alloy ΔW includes all of these main and side reactions. Especially, a part of Cu_2O freed into the sludge can go through a strong oxidizing dissolution depending on the condition of the solvent (the amount of dissolved oxygen present, for example), further complicating the calculation. Therefore, in order to make the applicaton of Equation (1), which was introduced for the pure copper anode, possible, the following two hypotheses were formulated.

(Hypothesis 1) The Cu_2O compounds found in the sludge remain stable for a long period of time without undergoing acid exosmosis.

(Hypothesis 2) All the oxygen in the sludge is said to be combined with Cu_2O compounds.

The amount of Cu_2O compounds contained in the total amount of a Cu-O anode dissolved can be easily calculated if the analytical value of the oxygen of that sample is known. In addition, the amount of Cu_2O compounds contained in the sludge (Cu^0+Cu_2O) derived from this anode can also be obtained in a similar manner. The difference between the two amounts is equal to the amount of Cu_2O dissolved via the anode process represented by Equation (2) ($\Delta W'$). In order to make Equation (1) applicable to the Cu-O anodes, the amount of electricity used in the above mentioned process (2) (I_2)

is subtracted from the total amount of electricity circulated (I_1), as well as subtracting $\Delta W'$ from the total amount of copper anode dissolved ΔW, and these corrected terms are substituted into Equation (1). That is,

$$\Delta W - \Delta W' = \frac{63.54 \times (I_1 - I_2) \times (100 + b)}{2 \times 100}, (g) \quad \cdots\cdots\cdots\cdots (5)$$

Furthermore, the calculation of b-value for cases in which the heat treatment if applied to the Cu-O anode is very difficult due to the fact that the Cu_2O phase is partially converted to the CuO phase and that this goes through the acidic exosmosis readily. Therefore, even through it is a rough supposition, it was decided to use Equation (5) by hypothesizing that such phase conversion did not take place.

3. EXPERIMENTAL RESULTS

3.1 Observation of the Structure

In the first place, the results obtained from observations made on untreated Cu-O alloy samples regarding the manner in which the structure changes over a range of typical oxygen levels are shown in Fig. 1.

With solidification, the metallic copper (the white section) was thought to be first formed, followed by the black eutectic (Cu^o+Cu_2O). As the oxygen level was raised, the eutectic was found to gradually become predominant, and eventually reached the eutectic point. Even though the eutectic point of Cu-O is said to be in the vicinity of

[O] = 3,900 ppm according to the reference (4), judging from Fig. 1 it seemed to be in the vicinity of [O] = 5,300 ppm (sample Cu 5). In any event, since finding the correct eutectic point is not the main aim of this research, the eutectic point was tentetively set at [O] = 5,300 ppm in order to continue with the following discussion.

When the oxygen level was further increased beyond the eutectic point, the Cu_2O arborescent structure that had been formed in excess in combination with the eutectic structure was found to be getting gradually more prominent (samples Cu 6 and 7).

On the other hand, the nature of the structural changes obtained when heat treatment was applied to the five samples of Fig. 1 is given in Fig. 2. When the two figures were compared, it was clear that the crystalline granules became markedly more coarse as a result of the heat treatment and that a substantial loss of the Cu_2O phase from the granular state was brought about. In addition, the reactivity of the surface of a treated sample was found to be increased a great deal to the extent that it was observed that immersion in a fairly weak etching solution (10 % ammonium pyrosulphate) for even a few seconds tended to cause excessive corrosion. Furthermore, numerous pits were observed on the etched surface. This is another characteristic that is not observed with untreated copper samples.

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In the hypoeutectic (Cu^{o}+E) region, the Cu_2O phase is in fact substantially lost from the granular state by the heat treatment, as stated above. However, when X-ray diffraction analysis was performed on a fresh surface of one such sample, it was confirmed that the Cu_2O phase was still remaining mixed in with the CuO compounds that were presumed to be newly formed by the heat treatment. A host of them is probably scattered among the crystalline granules as extremely small granules. Moreover, although it was not determined satisfactorily in this study what changes were brought about on the eutectic structure exhibited by the Cu 5 sample as a result of heat treatment, or to what new eutectic point the changed structure was shifted, a trace of the eutectic could be detected in the Cu 4 sample of Fig. 2. On the other hand, in the hypereutectic (E+Cu_2O) region, even 56
though some decrease in the Cu_2O formed in excess was seen as a result of heat treatment, some was confirmed to be still remaining (samples Cu 6S and 7S).

3.2 Determination of Reducing Current Density of Cu_2O Phase

Experiments to confirm from the standpoint of electrochemistry the cause of the phase conversion represented by $Cu_2O \longrightarrow Cu^{o}+CuO$, which is considered to be brought about by the heat treatment, were conducted.

When electric potential scanning is performed in the cathode direction under suitable conditions using a copper anode sample whose surface has been polished to a mirror-like

finish, a sharp peak that corresponds to the reduction of the Cu_2O phase is observed at -0.42 V vs. Hg/Hg_2SO_4(s). The i_{p,Cu_2O} values for the Cu-O alloy samples, before and after the heat treatment, determined using this method are shown in Fig. 3 as a function of oxygen level (solid line). For comparison, the results of similar determinations conducted on a series of samples in which only the oxygen level of some actual crude copper [a] was varied in a wide range were also combined and shown in Fig. 3 (dotted line).

What is clear from these results is that, with untreated samples of either Cu-O alloys or crude copper containing impurities, the reducing wave current that can be measured is shown starting in the vicinity of [O] = 850 ppm. On the other hand, when heat treatment is applied, the Cu-O sample starts to show the reducing wave around [O] = 3,000-4,000 ppm and continues to increase in a rectilinear relationship to the oxygen level, whereas the crude copper never shows the reducing wave for the entire range of oxygen levels studied.

The following points of interest are obtained when these experimental facts are compiled.

1) The fact that the conversion of the Cu_2O phase into the granular phase first becomes prominent when the oxygen level of Cu-O alloy reaches 850 ppm was clarified by the structural observations made in this study and this is in

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a) See Reference 5) for the basic structure.

agreement with the findings of reference 4). On the other hand, of the reactions taking place when electric potential scanning is performed in the cathode direction with a copper electrode in the copper electrolyte, one is the reduction of the Cu_2O phase, and the other is the gradual coating of the surface of the test electrode with the cathode copper film that is formed at the same time. These are two competitive reactions. In this instance, it is assumed that the signals of the reducing electric current are emitted mostly by the Cu_2O phase that is being formed into the granular state in mosaic fashion. Even though extremely small Cu_2O granules do exist among the crystalline granules, they are thought to be coated by the electrolytic copper film before they have a chance to give reducing signals. This hypothesis seems to explain well the fact that the slope of the rectilinear line starts to rise around [O] $\fallingdotseq$ 850 ppm.

2) Above the oxygen level of 850 ppm the $i_{p_{Cu_2O}}$ value for the Cu-O alloy is somewhat higher than that for the crude copper, regardless of the oxygen level. This must be due to the union of certain kinds of impurities contained in the blister copper (Ni and Pb, for example) with some anode oxygen.

3) The application of heat treatment to the Cu-O alloy samples results in the clear emission of reducing wave peaks starting in the vicinity of [O] = 3,000-4,000 ppm. Sample Cu 48 (a trace of eutectic structure is detected) 57

shown in Fig. 2 is included in this oxygen concentration range.

4) The reason for the fact that the reducing wave is never emitted by the heat treated crude copper until its maximum oxygen level (7,200 ppm) is reached is guessed to be due to the formation of oxides between elements, such as Ni and Pb, during slow cooling, a process which consumes most of the oxygen available. As expected, the presence in large quantitiy of substances, such as NiO and PbO_2, in the slime obtained from the electrolysis of heat-treated crude copper was observed by experiments[3] conducted separately. The PbO_2 phase is not normally found in the slime formed by untreated crude copper.

3.3 Dissolution Behaviour

Dissolution experiments using a series of Cu-O anodes before and after the heat treatment were conducted to obtain anode current efficiency, amount of sludge formed, and b-values according to Equation 5. These results are given in Figs. 4, 5, and 6 as a function of oxygen concentration.

The anode current efficiency was found to increase rapidly, along with an increase in oxygen level, within the hypoeutectic region. This increasing tendency was found to continue until the maximum (around 11 %*) was reached just before the eutectic point, and was found to decrease suddenly

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* Translator's note: Seems to be a typographical error. Should be 111 %.

to 105 % right after that. Once in the hypereutectic region, it was found to continue with a substantial increasing trend (however, not as sharp as that shown in the hypoeutectic region), along with the increase in the oxygen level.

Such behaviour was totally unexpected.

On the other hand, when the heat treatment was applied, the relationship between anode current efficiency and the oxygen concentration mentioned above was even more greatly changed. (Fig. 4).

The relationship of the amount of sludge formed to the oxygen concentration was found to show behaviour that is very similar in form to the situation described above (Fig. 5). The effect of heat treatment was also found to be great. That is, the sludge formation rate was greatly reduced for the entire range of oxygen levels studied. It was observed that, although with samples prepared by simply remelting and casting the electrorefined copper, [O] = 100 ppm, the sludge formation rate even after the heat treatment was found to be around 1.8 %, which is not very different from that without the treatment, the sludge formation rate was found to be considerably decreased if more oxygen was made available to these samples as well as applying the heat treatment. Especially with [O] = 3,900 ppm (sample Cu 48) the minimum value (0.07 %)[b] was recorded.

b) This particular sludge contains, though in small quantity, copper sharps that were clearly freed directly from the anode, thus an even smaller value would have been obtained if this amount was removed. Moreover, such copper sharps were never observed in other samples.

On the other hand, the oxygen-proofness of b-value was found to be similar to the above behaviour (Fig. 6). It was again confirmed that the effect of heat treatment is great in this instance also.

3.4 External Appearance of Sludge Formed

All sludges formed by the electrolysis of untreated Cu-O alloy anode were deeper brown than the fine copper powder formed by the electrolysis of pure copper. This is due to the Cu_2O phase content. Furthermore, as expected, the brown colour became more intensified as the oxygen level was increased.

In contrast to this, with the heat-treated Cu-O anodes, a sludge the color of which was a combination of brown + black was formed. This observation seems to support the possibility of a partial conversion of the Cu_2O phase to the CuO phase within the anode structure caused by the heat treatment consisting of annealing + slow cooling. The presence of the CuO phase was in fact confirmed by the X-ray diffraction analysis of the sludge. Particularly, the value of Cu:O $\fallingdotseq$ 63.54:14, which is close to the stoichiometric ratio, was obtained as a result of chemical analysis done on the sludge formed by the sample Cu 4S, which showed the minimum sludge formation rate.

4. DISCUSSION

From the experimental facts stated above, it became clear that the effect of the oxygen level contained in the

copper anodes on their dissolution characteristics was much greater than had been expected. Their dissolution behaviours were also found to be greatly affected, in particular, depending on the type (hypoeutectic, eutectic, hypereutectic) of the metal structure. Furthermore, the behaviour at the eutectic point is specific.

Although it is difficult to find clear explanations on these points just from the results of this study, explanations of the nature of the changes, such as shown by the b-value of Fig. 6, will be attempted below.

In the hypoeutectic region, mixed in with the metallic copper phase, the Cu_2O phase becomes more predominant as the oxygen level is increased. Electrolysis is then performed on the alloy anode consisting of these two phases by loading it with a fixed current density. If observed microscopically, the answer to the problem of whether the load current is distributed evenly among any part of the anode structure or if a situation exists in which the current passes more readily through the Cu^0 phase is still guesswork. However, if the difference of the electric conductivity ratio between Cu^0 and Cu_2O (40 times), as reported in reference 6), was applied here, it cannot be said that "partial preponderance" is totally impossible. If this is happening within the copper anode structure, then the current density of the section where the Cu^0 phase is in contact with the copper electrolyte would naturally be higher

than the mean value of the current density loaded to this anode. In this way, it is believed that such a tendency would be increased as the Cu_2O phase becomes gradually more predominant within the structure. As a result, the polarizing potential of the "microcopper anode" would also be raised accordingly, and this would facilitate the monovalent dissolution of copper.

$$Cu^0 \rightarrow Cu^+ + e^- \quad E^\circ = 0.521 \text{ V vs. N.H.E.}$$

As a result of the gradual rise in the Cu^+ ion concentration being dissolved near the surface of the microcopper anode, the equilibrium of the disproportionate reaction that follows ($2Cu^+ \rightleftharpoons Cu^0 + Cu^{2+}$) would be shifted to the right. The result of this is synonymous with the increase in the amount of copper powder (i.e. sludge) formed (increase in b-value), and these tendencies are in agreement with the dissolution behaviours of Fig. 5 and 6.

Following this reasoning, simple experiments were conducted to determine the effects of the load current density on the b-value. Pure copper anodes were electrolyzed for 2 - 3 days using two current densities, 200 and 500 A/m^2, and when the b-values were calculated by weighing the amount of copper powder formed a tendency of the b-value to increase as the current intensity was raised was observed by the values 3.14 % and 4.52 %.

The actual values obtained for the determination of 58
the electric conductivity (% IACS) of samples Cu 3, Cu 4, and

Cu 5 used in this study were 87.5, 87.7, and 81.4 %, respectively, when the mean value was obtained for each set of 11.

5. CONCLUSION

As a result of investigations done on the dissolution behaviours of Cu-O binary alloy anodes whose oxygen content was varied in a wide range, the following main conclusions were obtained.

(1) The effect of anode oxygen, as it is called the "internal factor", on the dissolution characteristics of copper anode is very great and differs greatly depending on the type (hypoeutectic, eutectic, and hypereutectic) of the metal structure.

(2) The nature of the changes in these dissolution behaviours is greatly changed with the application of the heat treatment consisting of annealing and slow cooling.

(3) A fact that this heat treatment caused a phase change, represented by $Cu_2O \longrightarrow Cu^{o}+CuO$, within the metal structure was confirmed electrochemically and by the chemical analysis of the sludge.

In addition, obtaining a more accurate "true eutectic point" is considered possible by focusing attention on the uniqueness of the dissolution behaviour just before and after the eutectic point and by pursuing closely the relationships, such as one between the anode current efficiency and the oxygen level, using a series of samples

consisting of Cu-O alloys whose oxygen levels are prepared in smaller intervals in the vicinity of the eutectic point.

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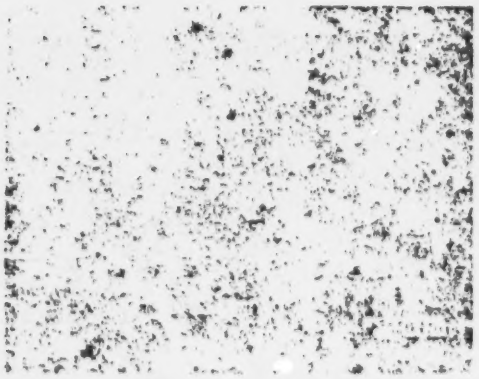
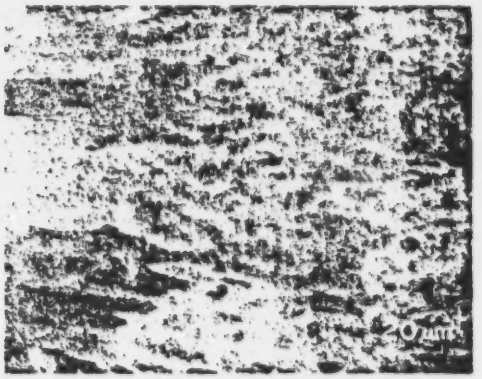
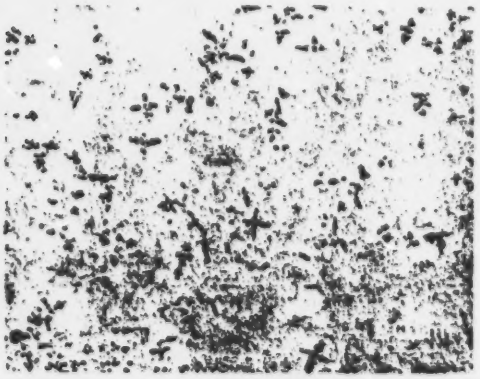
Cu 3 O = 2,400 ppm



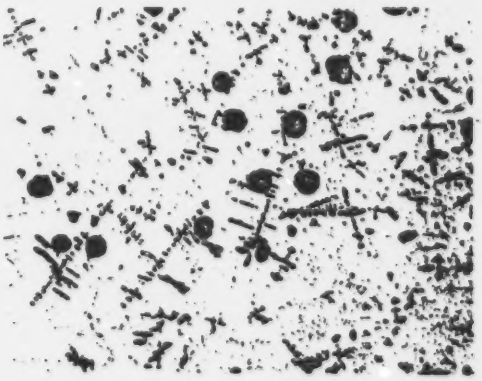
Cu 4 O = 4,800 ppm



Cu 5 O = 5,300 ppm

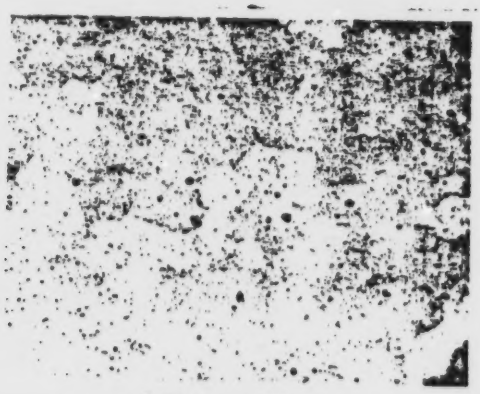


Cu 6 O = 7,300 ppm

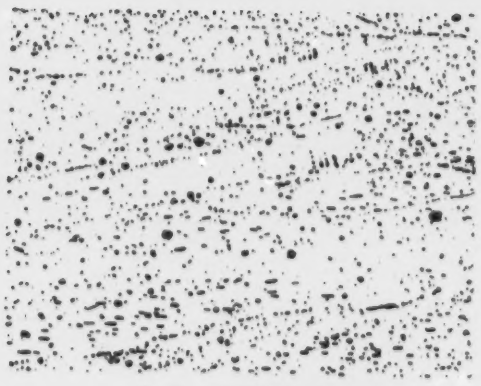


Cu 7 O = 8,800 ppm

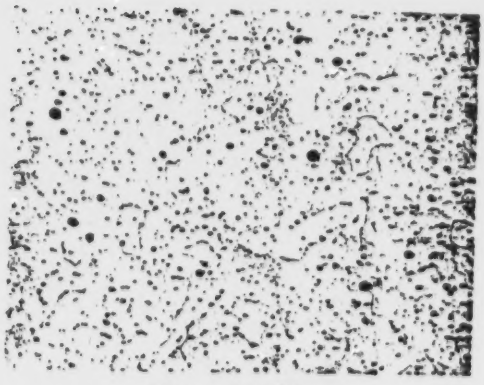
Fig. 1 Photomicrographs showing the effect of oxygen level upon microstructure of Cu-O alloys.



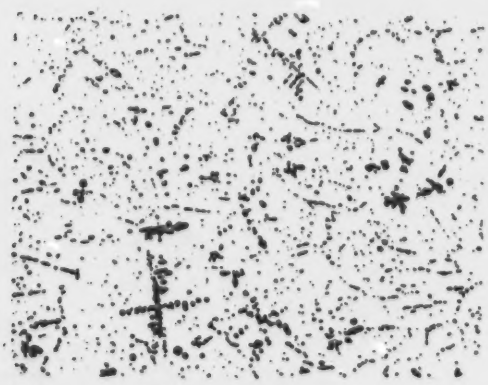
Cu 3S O = 2,300 ppm



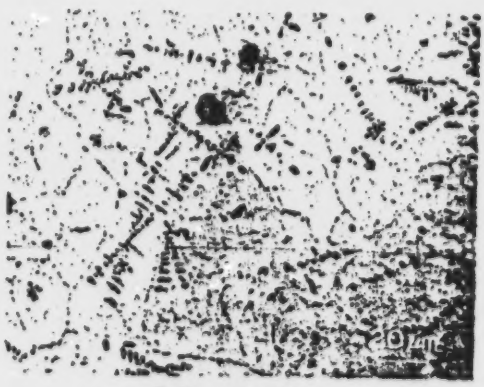
Cu 4S O = 3,900 ppm



Cu 5S O = 4,900 ppm



Cu 6S O = 6,500 ppm



Cu 7S O = 9,200 ppm

Fig. 2 Photomicrographs of Cu-O alloys after heat treatment.

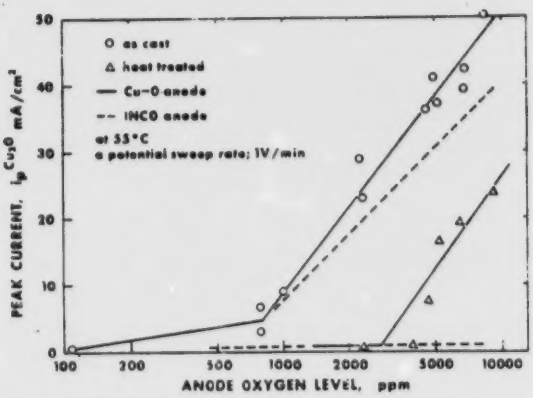


Fig. 3 $I_p^{Cu_2O}$ versus anode oxygen level: effect of heat treatment.

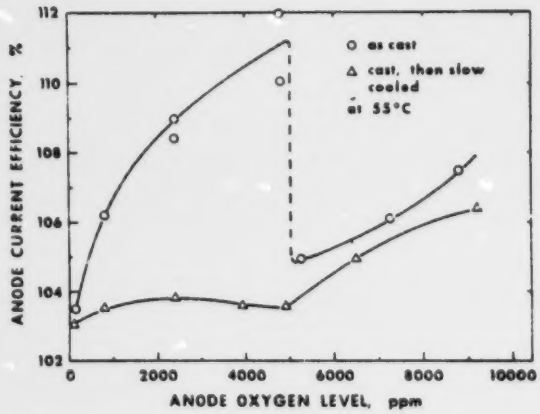


Fig. 4 Effect of anode oxygen level on the anode current efficiency of Cu-O alloys with and without heat treatment.

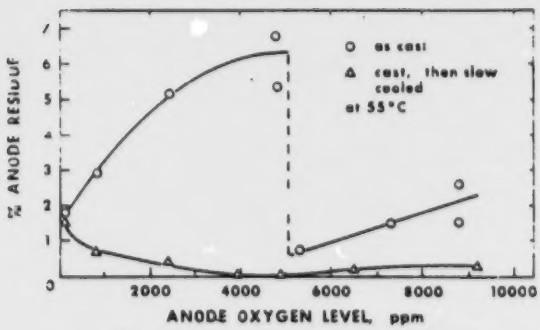


Fig. 5 % anode residue versus anode oxygen level.

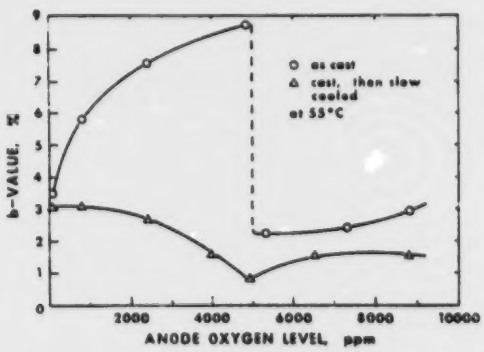


Fig. 6 Effect of anode oxygen level and of heat treatment on b-value.

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A PHASE CONVERSION $Cu_2O \rightarrow CuO + Cu^0$ OCCURRING IN THE MATRIX OF COPPER ANODES DURING THE ANNEALING/SLOW COOLING PROCESS*

97(37)

-- Anode Passivation in Copper Refining (9th Report)

by

Shin'ichiro ABE[1] and Sakichi GOTO[2]

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A certain heat treatment (annealed at 1,000°C, followed by slow cooling) was employed to various kinds of commercial copper anodes in an attempt to increase their dissolution activity in a copper electrorefining electrolyte.

It has been observed that such heat treatment brings about a drastic change in the microstructure as well as a substantial disappearance of Cu_2O phase from the grain boundaries. Both electrochemical and X-ray diffraction analyses have confirmed that a phase conversion $Cu_2O = CuO + Cu^0$ surely occurs in the matrix of copper anode so heat treated.

The results of dissolution experiments also appear to indicate that;

1) The heat treatment results in a great enhancement in the dissolution activity of copper anodes to such an extent that it can hardly be passivated under conventional Cu ER conditions, and
2) The sole employment of annealing (with no subsequent slow cooling) increases the dissolution activity but a little.

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I. INTRODUCTION

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Commercial copper contains oxygen whose action raises the level of the copper's dissolution activity. However, this positive effect sooner or later becomes a negative effect, because for one thing, the amounts of Cu_2O compounds which separate towards the anode slime layer increase correspondingly with the increase in amounts of oxygen. That is, the

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slime layer becomes thicker and denser, and the tendency to passivation increases.[1]

Thus the "accelerant" oxygen remains in the crude copper; however, if this adverse effect related to the Cu_2O phase can be eliminated, the dissolution activity of the crude copper anode may be expected to increase. To bring about this state, one effective measure may be to convert the Cu_2O phase already existing in the anode to the CuO phase. Even if the CuO phase, different from the Cu_2O phase, separates into the anode slime, it does not accumulate there for long, and may be thought to dissolve readily through the simple dissolution reaction $CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$, which does not even require an oxidant (for example, dissolved oxygen). As a result, the porosity of the slime layer increases, while it becomes thin at the same time. This facilitates the diffusion of copper ions from the anode surface into the solution, and so may be thought to aid greatly in decreasing the passivation tendency.

The present study examines various heat treatment conditions permitting this phase conversion to occur. It has been ascertained that under appropriate conditons, at least one part of the Cu_2O phase definitely converts to the CuO phase; this was determined by X-ray diffraction techniques, observation of structure, and electrochemical techniques; the results are herewith presented.

2. HEAT TREATMENT METHOD

Fig. 1, a phase diagram of a Cu-O binary alloy,[2] shows that the boundary of the stabilization area for both the Cu_2O and the CuO phases is around 375°C. Conditions when amounts of oxygen are below 5,000 ppm

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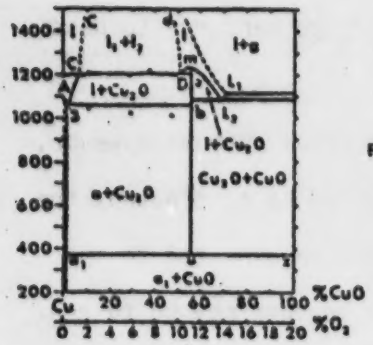

Fig. 1 Phase diagram of a Cu-O binary system.

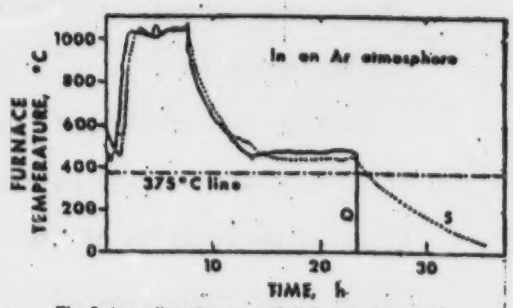

Fig. 2 Annealing plus controlled slow cooling processes employed to various copper anodes.

are the chief concern in copper electrolysis, but they are not clear from the diagram. In the present study, testing was begun by holding the crude copper materials at 460°C for a lengthy period, to examine the question of whether or not a conversion to the CuO phase could occur. In heat treatments effected on a laboratory scale, all the samples were small pieces of an appropriate size removed from the crude copper. With a view to raising the activity of diffusion within the structure of the oxygen and other impurities on the anode, heat excitation was first effected at around 1,000°C; the furnace temperature was then slowly lowered to about 460°C and held there for a lengthy period (Fig. 2). After this, one set of samples was submitted to quenching (abbreviated as Q treatment); another set underwent slow cooling and when the temperature was lowered to about 50°C, it was removed from the furnace (S treatment). The holding for a considerable length of time in the stabilization area of the CuO phase ($<375^{\circ}C$) was for the purpose of comparative study, to see how essential this is in raising the effectiveness of conversion to the CuO phase.

Furthermore, the samples used in heat treatment in this study, effected in an argon atmosphere, are commercial coppers of 13 types obtained from 9 copper companies, as used in a previous report[3], and also samples of a series adjusted to a wide range of the oxygen levels of INCO crude copper.

3. EXPERIMENTAL RESULTS

3.1 Changes in metal composition

First, observation of structure was made on all the crude copper samples having undergone S and Q treatments. As a result, it was observed that no matter which treatment was used, and regardless of the distribution of anode impurities, changes such as the following occurred:

(1) Conspicuous enlargement of crystallized particles

(2) Actual decrease of the excess Cu_2O phase which has separated out in the grain boundaries.

In addition, Table 1 indicates, for several classic samples, that no essential change occurred in the chemical compositions before and after heat treatment.

Table 1 Chemical compositions of various copper Anodes with and without heat treatments.

Anode	Heat treatment	Impurity level (ppm)								
		O	Ni	Pb	Sn	As	Sb	Se	Te	Ag
G-O	None	1700	4640	83	25	45	5	371	49	352
	S	1750	4600	80	18	41	6	360	68	340
	Q	1690	5000	60	22	44	5	365	62	300
G-6	None	5000	5000	80	15	31	3	340	79	330
	S	4900	5000	60	17	38	6	335	63	350
	Q	4900	4600	73	16	40	5	348	68	365
D	None	1500	930	1174	227	57	130	75	9	277
	S	1600	900	1050	200	38	190	60	17	250
	Q	1610	1000	1210	240	42	120	67	13	220
E	None	2300	1470	1320	28	67	160	46	2	197
	S	2100	1500	1250	28	44	200	40	11	230
	Q	2200	1450	1350	20	50	200	53	10	190

The results of electron-microscope observation of 3 types of crude copper (B, K, F), whose oxygen contents are respectively 600, 1,600 and 3,100 ppm, are presented in Figure 3 (untreated), Fig. 4 (S treatment), and Fig. 5 (Q treatment). In these Figures, a = crude copper B, b = crude copper K and c = crude copper F.

In the anode casting process, first the white copper portion is separated; then eutectic crystals ($Cu + Cu_2O$, black portion) form. The Cu_2O

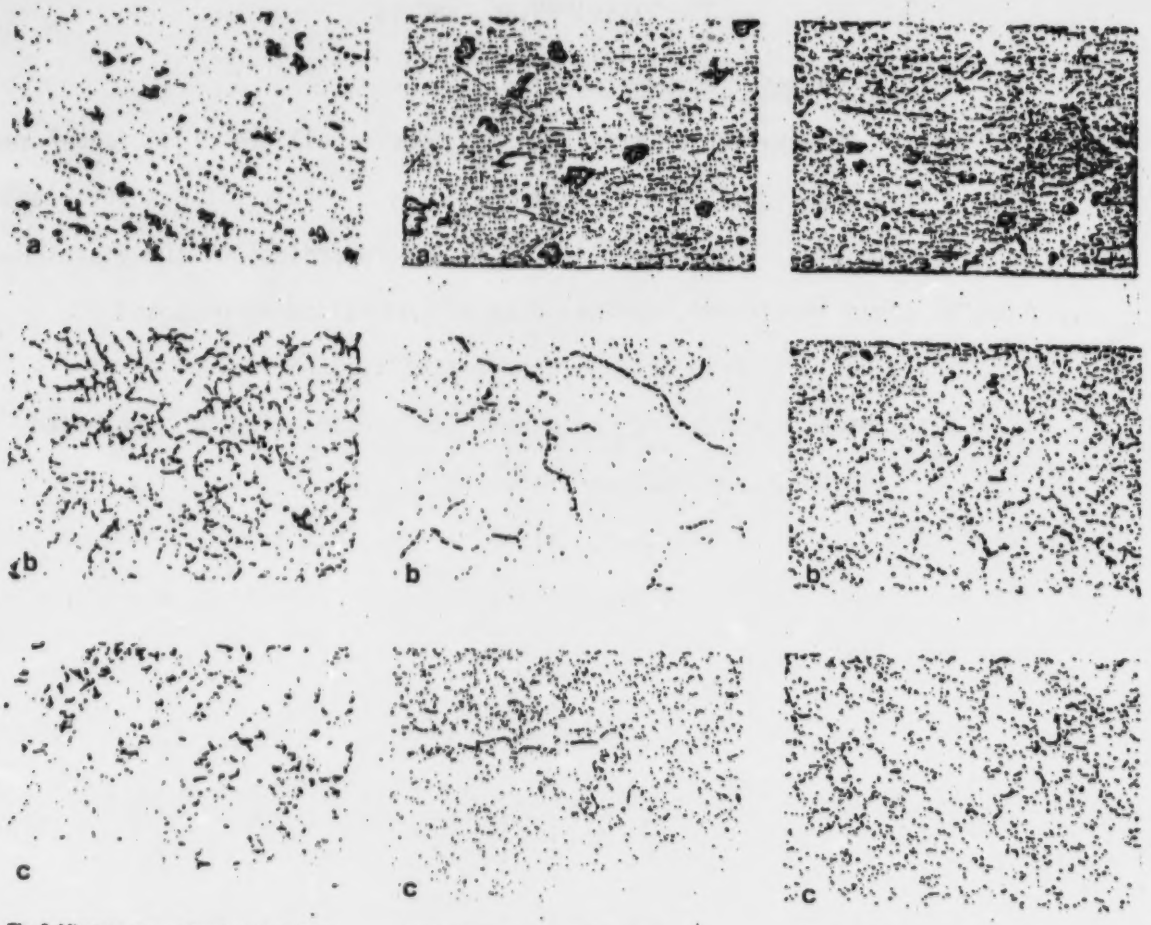

Fig. 3 Microstructures showing the polished section of each of copper anodes B(a), K(b) and F(c). (Untreated)

Fig. 4 Microstructures of copper anodes B, K and F with S treatment.

Fig. 5 Microstructures of copper anodes B, K and F with Q treatment.

phase, besides separating out into a mosaic pattern on the grain boundaries, is dispersed as extremely fine particles within the crystallized grains. After annealing and slow cooling, if the furnace temperature is brought to 460°C and held there for a long time, a process of gradual enlargement of minute Cu_2O particles may be expected. When quenching from 460°C is carried out, the reaction $Cu_2O = Cu^0 + CuO$ occurs in part, and it may be supposed to occur clearly, to a considerable extent, when slow cooling is carried out after that from 460°C. For both S and Q treatments,

numerous pits of rather large size appear over the entire etching surface of the crude copper samples (Figs. 4 and 5), but on untreated samples, pits are not observed: this is one of the special characteristics of the treatment. It could not be determined what kind of phase existed before etching on the portions where pitting occurred, but it may perhaps be considered as having the CuO phase, newly produced by heat treatment, as its principal component. This is because the CuO phase undergoes chemical erosion at a rate incomparably faster than the Cu_2O phase. For example, untreated copper samples could not be properly etched unless a strong solution of nitric acid 1: water 2 was used, but as a result of using heat treatment, immersion of scarcely 1 or 2 seconds was sufficient, even with a 10% ammonium pyrosulfate aqueous solution which has a relatively mild etching power. 99(39)

Now, to compare the results of S and Q treatments as described above: samples held at 1,000°C for a long time (about 7 hours) were directly submitted to oil quenching at room temperature. Fig. 6 presents the results of the structures thus obtained. It was seen that in samples B, F and K which underwent annealing only, the same structural changes as those above described occurred, such as enlargement of crystallized particles and substantial disappearance from the grain boundaries of the Cu_2O phase. However, what is notable is that the sensitivity to etching is about as low as that of untreated copper, and also, pits did not appear in such great number on the etching surface; hence this case is very different from effecting heat treatment of the type "annealing plus slow cooling."

As possible support for these observations, crude copper anodes submitted to S and Q treatments all show a passivation time of over

200 minutes, while the passivation time for those undergoing annealing plus oil quenching showed only a twofold increase at most, compared to untreated anodes.[a] This suggests that heat treatment causes significant changes in composition, and that the substance in itself is not an essential factor in raising dissolution activity. It seems that the "slow cooling" after annealing may well be essential.

3.2 Determining the occurence of the phase conversion $Cu_2O \rightarrow CuO + Cu^0$

It was ascertained through X-ray diffraction and electrochemical techniques that the phase conversion $Cu_2O \rightarrow CuO + Cu^0$ definitely occurs in the composition of crude copper samples, by the annealing and slow cooling described in 3.1.

Fig. 6
Microstructures of copper anodes B, K and F with heat treatment of holding at 1000°C for 7 hours, then oil quenched.

(a) For untreated samples, 1-17 minutes over all the crude copper (REFERENCES, note 3).

(a) X-ray diffraction method: A number of samples, after heat treatment, were polished to a mirror finish and phase identification analysis was carried out along that plane using X-ray diffraction. As a result, the presence of a newly produced CuO phase, mixed in the Cu_2O phase, was ascertained.

(b) Electrochemical method: As previously reported in detail,[4] when the Cu_2O phase exists in sufficient amounts on the crude copper electrode surface, it undergoes cathodic reduction by the reaction $Cu_2O + Cu^{2+} + 2e^- \rightarrow 2\,Cu + CuO$, and shows sharp peaks in the vicinity of -0.42V vs. Hg/Hg_2SO_4. When the high-oxygen copper G-7 undergoes cathodic polarization, a Cu_2O reduction wave clearly appears, as for example in Fig. 7 (unbroken line). Next, when this sample is submitted to S treatment, a conversion towards the CuO phase is seen to have occured to a considerable extent, and the reduction wave peak is destroyed.(b) However, if Q treatment is applied, this reduction wave peak is not prominently reduced and does not reach the point of complete disappearance. It is not impossible to think, as in section 3.1, that as a result of Q treatment, a phase change has proceeded in part only.

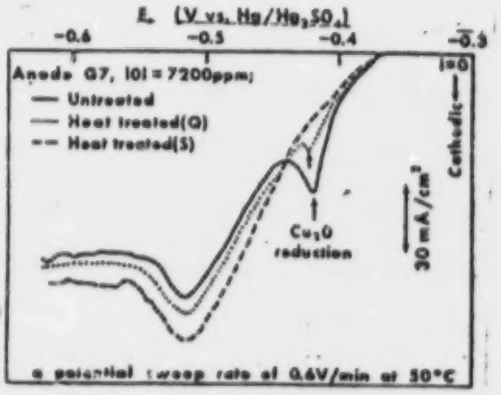

Fig. 7 → Cathodic polarization curves showing the substantial reduction in the peak current corresponding to $Cu_2O + Cu^{2+} + 2e^- \rightarrow 2Cu + CuO$ as a result of heat treatments S and Q of high-oxygen anode G-7.

(b) It was found from the results of X-ray diffraction that a part of the Cu_2O compound remains in fine particles within the crystallized particles. A detailed account of this phenomenon has appeared in a separate study (REFERENCES, note 5).

Here, it must be noted that a disparity between S and Q treatments was ascertained, as above, but from the viewpoint of compositional observation alone, almost no disparity is seen, as shown in Figs. 4 and 5.

4. DISCUSSION

In the electrolytic refining of crude copper anodes, the reasons 100(40)
for increased dissolution activity through the oxygen component include, as one confined to the area of estimates, the one-electron oxidation reaction in two stages:

$$Cu^0 \rightarrow Cu^+ + e^- \quad \text{(rapid reaction)}$$
$$Cu^+ \rightarrow Cu^{2+} + e^- \quad \text{(slow reaction)}$$

In the latter, some kind of catalytic action may be involved, accelerating the reaction towards the right. The fact that the anode oxygen, which should have a plus effect, exists as Cu_2O in the structure, was a problem (see Introduction); this point was scrutinized in the present study. Investigation was made on the possibility of at least one part of the Cu_2O changing phase to CuO, through appropriate heat treatment.

As for the reasons for increase in anode dissolution activity, it would be natural to pursue research on changes in the anode structure, and also on changes in the slime layer. For the former, it is true that a structural change occurs in the anode, accompanying a partial conversion of the Cu_2O phase to the CuO phase, but at present it is difficult to offer sufficient explanations as to why the dissolution activity of the anode is conspicuously raised. This remains a subject for further investigation.

If the slime layer is considered, the following phenomena occur. Upon electrolysis, the particles of CuO oxides present in the anode composition, whatever their size, separate from the dissolution surface, enter the

slime layer and settle there for a time. Then the slime layer begins to erode, and pores are produced where the CuO particles sooner or later disappear. No matter how small the pores, they occur in virtually countless number here and there in the slime layer, which has a three-dimensional structure. As a whole, in this type of slime layer, high porosity may be expected to occur. At the least, in comparison with the porosity of a slime layer which develops without any CuO particles having entered in the first place, this expectation may not be wide of the mark. If this occurs in fact, the diffusion of copper ions takes place smoothly, and passivation is not easily reached; moreover, the vat pressure tends to decrease. Another test has determined that both are phenomenologically correct.[4]

Furthermore, if the amounts of oxygen in crude copper are gradually increased, the excess Cu_2O phase starts to separate out in the grain boundaries from about 850 ppm, but in response to this, the $i_p^{Cu_2O}$ also separates distinctly from this oxygen level, and after that, along with an increase in amounts of oxygen, there is a steady linear increase. This is indicated in Fig. 8, but on the other hand, if S treatment was applied, the $i_p^{Cu_2O}$ value extended over the entire area of the oxygen concentration, and was practically at zero (unbroken line). When the anode

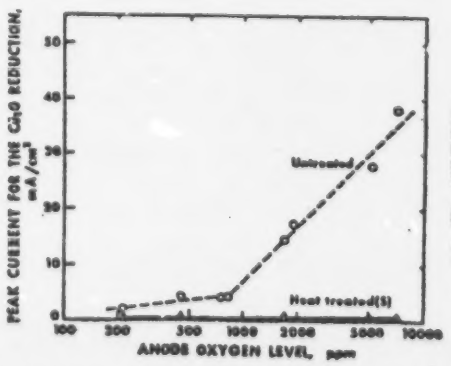

Fig. 8 i_p Cu_2O versus anode oxygen level: effect of heat treatment S.

was a Cu-O alloy[c], its appearance changed, and even when S treatment was applied, i_p Cu_2O started to appear from about [O] ≒ 3,800 ppm, and after that point there was a linear increase with the amount of oxygen.[5] This disparity for crude copper and Cu-O anodes may be explained as follows: The crude copper contains metallic impurities such as Pb and Ni, and through their relative oxygen affinities, the oxygen atoms, bound to Cu_2O may be removed. This occurs in the slow cooling process; as a result, much Cu_2O is consumed, and in its stead, metal oxides such as NiO and PbO_2 are newly produced.[6] On the other hand, in the case of Cu-O alloy anodes, a marked separation of excess Cu_2O from around [O] = 3,800 ppm occurs there is no possibility for combination of the oxygen atoms with other elements.

5. CONCLUSION

To summarize the results of discussing the possibility of conversion to the CuO phase, through high temperature treatment of at least one part of the anode oxygen (existing as Cu_2O) which accelerates the dissolution activity of crude copper, the following conclusions may be made.

(1) If slow cooling is carried out after annealing at a high temperature, (about 1,000°C), the reaction $Cu_2O \rightarrow CuO + Cu^0$ occurs in the composition of crude coppers of all kinds. At the same time, compositional changes such as marked enlargement of crystal particles, and disappearance of Cu_2O from the phase grain boundaries also take place.

(2) A partial conversion occurs after lengthy holding at 460°C, even if quenching (Q treatment) is effected, but if this is followed by slow cooling from 460°C towards room temperature (S treatment), the efficacity

(c) A clean anode with almost no other impurities.

of this conversion may be thought to increase. However, despite the difference, the appearance of the compositional changes in both cases is very similar, making the disparity hard to discern.

(3) The change incurred by the composition of the crude copper samples submitted directly to oil quenching after only holding for a lengthy period at 1,000°C, is approximately the same as for S and Q treatments, as above. However, the passivation times of anodes of this type, compared to untreated ones, showed only a twofold increase at the most. Thus, structural changes, brought about by annealing, is not the essential factor in decreasing remarkably the passivation of crude copper anodes. Rather, it may be thought that slow cooling after annealing is a substantial factor.

Lastly, for the results of dissolution experiments carried out on various types of crude copper anodes submitted to heat treatment, a further report will be published. [6] 101(41)

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Dissolution Characteristics of Thermally Activated Copper Anodes*

- Anode passivation in copper refining (10th Report) -

by

Shin-ichiro ABE[1] and Sakichi GOTO[2]

Various commercial copper anodes were heat treated by an annealing/slow cooling process, and their dissolution characteristics were extensively examined using copper electrorefining electrolytes.

The results obtained indicate that the following major beneficial effects could be achieved through this heat treatment;

1) The dissolution activity dramatically increases, which is responsible for the combined effect of anode slime layer becoming significantly more porous, thus making the diffusion of Cu^{++} ions much easier, and also of the anode itself being rendered very active.
2) As its consequence, cell voltages of the so heat treated anodes become significantly lower than those obtained for the untreated,
3) Slime fall dramatically decreases by 24 to 43% for all the anode samples tested, and
4) The colloidal (or amorphous) nature of anode slimes is considerably reduced, which results in a reduced incidence of the suspended slime particles to be formed in copper electrolyte, which, in turn, reduces a risk of the copper cathodes being contaminated with such impurities as As, Sb, Bi, Se etc.

It has also been shown that the distribution of slime-forming compounds dramatically changes as a result of this heat treatment.

1. Foreword

We examined the dissolution characteristics of various crude copper anodes which had been thermally activated as already explained[1)] (the Q-treatment whereby the anode is kept for about 7 hours at a

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temperature around 1,000°C, then brought slowly to around 460°C and maintained at this temperature for about 10 h after which rapid cooling is performed; the S-treatment whereby slow cooling is pursued to room temperature).

2. Tests and results

2.1 Passivation time

We first examined the effect of the $Cu_2O \rightarrow CuO + Cu^\circ$ phase transformation taking place within the texture of crude copper, and of the noticeable crystal grain coarsening consequent to the heat treatment on the dissolution characteristics of the anode. The most direct way of finding a standard for knowing the proportions of dissolution activity changes is to measure the passivation times (tp) of the heat-treated samples under given electrolytic conditions and to compare the values mutually.

We performed in advance for 24 h the anodization of various 4 cm x 12 cm x 1 cm samples and allowed the formation of a slime layer with a quasi-equilibrated thickness. Thereafter, we obtained with a current density of 400 A/m^2 the passivation in on-site electrolytes (50°C) containing 43 g/L Cu, 198 g/L H_2SO_4, 17 g/L Ni, 3.4 g/L Fe, 5.8 g/L As and a few impurities such as Bi, Sb. Table 1 shows the tp measurement values obtained with regard to several typical crude copper samples.

We see first from Example 1 that regardless of the type of anode the effect of high-temperature activation treatment is remarkable and that with both the Q- and S-treatments the dissolution activity rises to a level such that passivation is very unlikely under usual

electrorefining conditions. Example 2 also shows clearly that even when the level of oxygen which inhibits anodic dissolution rises very high, the tp values increase remarkably because of the present thermal treatment. We can also see that the effectivity is maintained even when the level of free sulfuric acid in the electrolyte becomes very high (Example 3).

2.2 Electrochemical examination

Using several electrochemical methods, we performed examinations in order to understand better the fact that "annealing + slow cooling" raises so remarkably the dissolution activity of all types of crude copper anodes.

2.2.1 Anodic polarization curve

We measured the anodic polarization curve of the anode G-6 which among the samples used in the present study is the most easily passivated, and examined the effect of thermal treatment.

We gave a mirror-like finish to the exposed surfaces (1.3 cm x 1.3 cm) of various parallelipiped electrodes embedded in epoxy resin. Immediately after washing with water and degreasing, the potential was scanned (0.06 V/min) in a standard copper electrolyte (40 g/L Cu, 200 g/L H_2SO_4, 20 g/L Ni, solution temperature of 50°C). This cyclic voltammetry operation was performed between the natural electrode potential of the various sample electrodes and 0.1 V (vs. Hg/Hg_2SO_4). Fig. 1 shows the first scanning (curve a), the fifth scanning (curve b) as well as the measurement results performed following 24 h of electrolysis performed immediately thereafter at

200 A/m^2 (curve c). We see that the effect of the S-treatment is extremely strong.

It is quite normal that the highest current density value vs the $Cu^{\circ} \rightarrow Cu^{2+} + 2\ e^{-}$ anodic dissolution decreases gradually as the electrode surface becomes covered with a slime layer. However, the degree of decrease is much smaller with regard to heat-treated copper (graph b). Moreover, even after the formation of a relatively thick coat of slime layer through 24 h electrolytic treatment, the highest dissolution current density value of these particular anodes is greater than the values observed in anodes with an untreated copper surface whose slime layer is not overly thick (CV # 5, graph a). p. 254

The anodic polarization curve of Q-treated copper (not shown in the graph) shows a behavior intermediate between no-treatment and S-treatment.

2.2.2 Current-time curve

Aside from the change in slime layer structure as compared to untreated samples (actually, more porous and thinner), the rise in dissolution current with regard to thermally treated copper referred to in the former section seems to be an overall effect of the increased dissolution activity of the anode itself. With regard to the latter, we may, as already explained[1], estimate that it is because the reactivity at heat-treated copper etching time exhibits an abnormal rise. As for the former, we intend to publish very soon the results of detailed examinations.[2]

In this section we use again the anode G-6 and perform a series of current-time curve measurements with regard to the 3 conditions of

no-treatment, S- and Q-treatments. The test solution and solution temperature are the same as for the polarization measurement conditions in the former section. However, the set potentials are 50 mV more noble (around -0.31 V) than the natural electrode potentials* of the respective test electrodes. The results are shown in Fig. 2. It is clear that while the electrode surface is still quite fresh ($t \to 0$), the dissolution current increases in the S > Q > no-treatment order. Such tendency, when there is almost no slime layer formation yet on the surface of the electrode, seems to support the view that the dissolution activity of the anode itself was raised through the heat treatment.

We performed similar measurements on pure copper anodes (dotted line). At the beginning of electrolysis, the dissolutinn current was at a level fairly lower than that of the 3 states of the G-6 electrode. However, in the case of this pure copper anode which, practically speaking, develops no slime layer, there is almost no attenuation accompanying the passage of the subsequent electrolysis time, and a constant level is maintained.[a)] With crude copper anodes which develop a slime layer, the dissolution current goes on decreasing with the passage of time. With untreated samples for instance, the course is in opposite direction to that of pure copper after only 1 min from electrolysis start. Similarly, with the Q-treatment too, the

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*Translator's note: The note c) hereunder with no c) reference sign in the text is placed here because of the similarity of words.

c) The natural electrode potential of heat-treated samples shifts by about 10 mV to a baser level when compared to the case of no-treatment in coper electrolyte.

a) From the strict viewpoint of daily units, the dissolution current was seen tending to drop. The reason is that the surface of the anode becomes gradually grooved through corrosion and fine copper particles accumulate in the grooves.

turn-around time is delayed somewhat longer but the tendency is the same. With the S-treatment (not shown in the graph) the dissolution current after about 10 min of electrolysis is somewhat lower than the level of pure copper anodes and regular stabilization was observed.

2.2.3 Critical current density

In order to obtain a standard to know to what extent the passivation of heat-treated crude copper anodes was unlikely during actual operations, we measured a series of passivation critical current densities.[b] The results obtained at a solution temperature of 50°C are arranged in Table 2.

With the exception of crude copper B which is very little prone to passivation, the crude copper anodes show generally values within the 170-220 A/m^2 range. If the current density is inadvertently raised, such values, so low that passivation is not quite impossible, increase significantly through the S-treatment. In spite of the used solution temperature of 50°C which is considerably lower than the average temperature (60°C) during actual operations, the no-passivation safe current density test values already reach the hardly imaginable high level of 300 A/m^2.

When comparing with others, the anodes (G-4 and G-6 as well as K and L) stay at a somewhat low level and this occurs (266-290 A/m^2) because the amount of contained nickel is extremely high and that the amount of oxygen is rather high. When cooling slowly p. 255 crude copper containing

[b] We first measured the passivation times (tp) while changing variously the current density (C.D.) and took as critical current density in the graph showing the plotting of the obtained tp^{-1} vs. C.D., the C.D. at the time when extrapolating to $tp \rightarrow \infty$.

high oxygen/high nickel, extremely stable NiO compounds are produced, and as these result in a slime layer with a considerably large volume. There seems to be a degree of "off-set" action.

2.3 Cell voltage

We chose 4 types of crude coppers and followed the time-course changes of the cell voltages when electrolyzing them respectively at 200 A/m^2, 300 A/m^2. We used synthetic standard electrolyte, and the electrodes were kept at a distance of 100 mm. The chosen crude coppers differ mutually in impurities distribution. Yet, as shown in the Table hereunder, the presence of oxygen and nickel in the materials is extremely different.

unit: ppm

Sample	Volume of oxygen	Volume of nickel
B	610	149
F	3,100	826
L	1,700	4,600
G - 7	5,000	5,000

Fig. 3 (200 A/m^2) and Fig. 4 (300 A/m^2) show respectively the test results when electrolyzing these samples (untreated, S- and Q-treatments) at a solution temperature of 50°C.

If we first watch the dissolution behavior of the untreated samples, we note that the proportion of time-course change of the cell voltage tends to increase in the B < F < L < G-7 order. This is because it reflects the increase in (oxygen + nickel) proceeding in the same order. Meanwhile, as a result of these high-temperature activation treatments, the cell voltage drops obviously while going through the entire electrolysis period. The values at initial electrolysis time

when there is virtually no slime layer formation are also low and this seems to mean that the activation polarization of the crude copper anode itself decreased considerably because of the thermal treatment.

2.4 Slime analysis

2.4.1 Changes in formation volumes

We electrolyzed various crude copper test pieces (4 cm x 12 cm x 1 cm) for 2-3 days in usual copper electrolyte 50°C, with a current density of 200 A/m^2, collected the entire amount of slime and weighed it after washing with water and drying.

When electrolyzing some crude copper under both no-treatment and thermal treatment conditions and plotting on the X and Y axes the respective slimes produced, if we suppose that there is no thermal effect, the points so obtained should proceed along the X = Y straight line. If to the contrary the thermal treatment has a great effect, to this extent there should occur a deviation from X = Y. Fig. 5 shows the plotting by this method of the obtained amounts of slime formation. The results with regard to the respective S- and Q-treatments are also included.

These results indicate that the volumes of slime formation decrease by an average of 43% with regard to the S-treatment for all crude copper samples. Although smaller with the Q-treatment, the decrease is still 25%. The chemical analysis of the slime demonstrates that the reason for the remarkable decrease in the volume of slime formation due to thermal treatment lies mainly in the decrease of copper compounds in the slime. Table 3 shows one example. Because of the thermal treatment, part of the Cu_2O in the anodic texture underwent a

phase transformation to oxide (CuO) which is of a type in which acid leaching is easy.[1)]

We performed this time similar tests on a series of samples whose amounts of oxygen in a given crude copper had been adjusted over a wide range. That is, we S-treated the INCO crude copper sample G-O-G-7[3)], and using the obtained volumes of slime formation as functions of the oxygen contents, we plotted these in Fig. 6 (solid lines part). For the sake of comparison we show at the same time in the graph the already reported[4)] data for a similar series of untreated samples (dotted lines part). A comparison betweeen the two reveals that the volume of slime formed decreases considerably over the entire oxygen range and that the main reason is that the copper contents in the slime decreased. As also shown in Fig. 6, the volume of nickel in the slime to the contrary increased through heat treatment because the formation of a stable NiO phase was promoted. This has been explained previously.[3)4)]

2.4.2 Slime compounds distribution p. 256

We performed phase identification based on the X-ray diffraction method with regard to the various slime samples obtained in the former section. The results are arranged in Table 4.[d)] It is obvious that on the whole, the distribution changes of the structural compounds due to heat treatment are extremely large. We will give one by one a few characteristic points revealed in Table 4.

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d)We showed the results only for the S-treated samples. An almost similar trend is seen among the Q-treated ones.

1) Copper compounds such as Cu_2O and Cu° which were established in the initial main phase or in the accessory phase become completely lost as a result of the heat treatment (crude copper K excepted). They are replaced by newly formed copper compounds of a different form such as $Cu_{2-x}Se$ and CuAgSe, or the amount increases by one degree[e] (crude coppers D and F excepted).

2) The unconfirmed phases (UI: unidentified phase) have completely vanished as a result of the heat treatement.[f]

3) The metallic silver phase (Ag°) appears more clearly.

4) The NiO compounds too become more dominant (crude copper L, D, F, K, L').

With regard to characteristic 2), UI is the main phase in the slime obtained by the electrolysis of sample G-O while CuAgSe is an accessory phase, and the other detected compounds were only very minor phases. In this connection, the chemical compounds (%) of this slime are 11.2 Cu, 2.2 Ni, 0.13 Pb, 0.24 As, 2.51 Ag and < 0.05 Bi. In any event, characteristic 1) seems to suggest that as a result of the heat treatment the $Cu_2O \rightarrow CuO + Cu°$ phase transformation is certainly

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e) Estimated from the height of XRD peak.

f) As they appear as a peak in the X-ray diffraction pattern, they seem to be some type of crystalline compound. Yet because of some reason (for example the cooling speed was too high at the anode casting stage), these compounds inside the crude copper texture become completely cooled before sufficient growth, and so may be existing while presenting a non-stoichiometric structure.

produced. Since, as explained above, the volume of the Cu_2O phase liberated from the dissolution surface of the copper anode decreases suitably, there is only a very slight occurrence of the $Cu_2O + H_2SO_4 + CuSO_4 + Cu^\circ + H_2O$ desequilibrium reaction inside the slime layer.[3] This is why in Table 4, the Cu° phase disappeared from the slime as a result of the heat treatment. p. 257

There are two types of silver compounds; viz., Ag° and CuAgSe. Observation 3) of the fact that the former is not produced from untreated copper but only and clearly through heat treatment is interesting. Regarding this phenomenon, there are two hypotheses. a) The Ag° phase present in the copper texture is made of very fine particles so that this is liberated without any change inside the slime and does not show well with the analysis sensitivity of the performed X-ray diffraction. b) The fine Ag° grains are masked within the slime layer by some amorphous (or colloidal) compounds so that the signals coming from Ag° are intercepted at X-ray diffraction time. It is also possible that as a result of (annealing + slow cooling), the silver particles inside the texture grew gradually in size. If hypothesis b) is correct we are given an important suggestion. That is, it could be that the colloidality disappears entirely from or decreases in the slime generated from heat-treated copper. In this case, heat treatment could help inhibit the formation of the slime (floating + suspended) generated during copper electrolysis (see next section).

2.4.3 (Suspended + floating) slime

This time we performed relatively large-scale electrolytic tests. We need 2 types of crude copper samples obtained again from the electrorefining companies A and C. The chemical compositions are given in Table 5. We kept these samples (12 cm x 17 cm x 3 cm) first for about 1 h at 950°C in a stainless box (16 cm x 28 cm x 6 cm) fitted with a lid while injecting slowly N_2 gas and transferred thereafter to slow cooling. To reach an oven temperature of 500°C we adopted the fast cooling speed of about 200°C/h. Thereafter to reach the vicinity of 100°C, we chose the relatively slow cooling speed of 10°C/h. We noticed virtually no sample surface oxidation but to be safe, the surfaces were finished by mechanical process before being used for the tests. Using an 18 L capacity electrolytic cell, we performed electrolysis for 7-8 continuous days under usual electrolytic conditions (200 A/m^2, 60°C, standard copper electrolyte). During the whole period, the solution was recycled by being made to flow through a by-pass at the rate of 5 L per hour so as to obtain a balanced solution composition. At the same time, the slime particles were captured with a filtering device (suspended + floating) placed properly on the by-pass route. The amount of matter captured was divided by the amount of solution in the total cycle. The value obtained was taken as slime concentration.

While crude copper A is characterized by fairly high contents of oxygen and nickel, the same contentes in crude copper C are so low that they are negligible. On the whole, the other impurities also seem to be well controlled in crude copper C. Of course such difference is reflected in the amount of slime formation. As shown in Table 5, B), the production is 18 mg/L for the crude copper A which is about 60% higher than for crude copper C. We see that because of the heat

treatment, there was a trend to considerable decreases in both. The rate of decrease from 11 mg/L to 4 mg/L in crude copper C is conspicuous. As expected, we also observe a considerable decreasing trend in total generation*. The results are shown hereunder together with the passivation times.

Anode	Treatment	Generation* volume (kg/t Cu)	Passivation time (min)
A	no treatment	5.7	2
A	slow cooling	4.7	80
C	no treatment	1.1	17
C	slow cooling	0.7	> 300

It is also most amazing that the quality of the electrodeposited copper is considerably raised through heat treatment (Table 5, C). The particularly remarkable fact is the conspicuous decrease in the concentration of silver. Simultaneously the quality of As, Sb, Bi, and of Se drops considerably. p. 258

2.4.4. Observation of the slime by electron microscope

This time, choosing a typical crude copper anode L, we electrolyzed untreated, S-treated and Q-treated samples and performed scanning electron microscopic observations of the slimes obtained. The results are shown in Fig. 7.

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*Translator's note: Meaning uncertain; the term means literally "maternity room".

We see that in the untreated samples (Photograph a) almost half of the particle cluster is occupied by extremely large lumps (150-200 μ). The other samples are composed of an aggregation of particles similar to sand particles apparently very diffusible, as evidenced by Photograph b (S-treatment) and Photograph c (Q-treatment). One may see that these large lumps seem to be collections of the small particles shown in Photographs b and c. In this case it is hard to explain well what agent plays the present "binder" role.[8] Be the matter what it may, these lumps seem to have enough strength to remain unbroken through water rinsing or washing with alcohol.

As a result of the above SEM observations, there remains a serious possibility that one may not draw the conclusion that the porosity of the slime layer formed on the dissolution surface of heat-treated crude copper increases.

3. Conclusion

We heat-treated (annealing + slow cooling) various types of crude copper samples and performed from various angles the examination of the dissolution characteristics of the same. As a result, the possibility was suggested that several electrolysis advantages might be derived from this heat treatment. The main benefits are as follows.

1) Regardless of the type of crude copper, the dissolution activity rises to such an extent that under normal electrolysis circumstances passivation becomes finally impossible. There is no need to worry about passivation even when loading a current density of at

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8) This may be some colloidal compound.

least 300 A/m^2 and tank house operations seem possible.

2) We saw that compared to untreated samples, the volume of slime generated from heat-treated crude copper is for all types of crude copper 24 ~ 43% lower as an average. The main reason is that the copper compounds (Cu_2O and Cu°) decreased inside the slime.

Furthermore, as a result of the heat treatment, the amorphism (or colloidality) of the produced anodic slime was seen to decrease. The slime particles diffuse very easily and do not coagulate so that the slime layer made from such particles is expected to be more porous.

4) Because of the result 3), the rate of slime (suspended + floating) formation drops sharply. As a result, the quality of the cathode copper rises remarkably. More particularly, the volume of silver loss decreases considerably. Simultaneously we saw that the levels of harmful impurities such as As, Sb, Bi and Se are brought down to a very low level.

5) When electrorefining crude copper treated at high temperature, the activation polarization becomes small so that the voltage of the cell drops. This is desirable from the viewpoint of power-saving.

Table 1: Passivation characteristics of copper anodes: effect of heat treatments

Example 1: Using anodes from various refineries.

Anode	Untreated	Passivation time, min	
		Treatment S	Treatment Q
B	94	> 200	> 200
D	17	> 200	> 200
E	12	> 200	> 200
F	11	> 200	> 200
K	3	> 200	> 200
L	1	> 200	> 200

Example 2: Using INCO anode (K) spiked with different oxygen levels.

Anode	O level (ppm)	Untreated	Treatment S	Treatment Q
G-2	450	14	> 200	> 200
G-3	820	7	> 200	> 200
G-6	5000	<1	> 200	130
G-7	7200	1	160	60

Example 3: Using anode G-6 with treatment S or Q, measured in the standard Cu electrolyte at varying H_2SO_4 level.

Anode	Treatment	Passivation time, min; at H_2SO_4 level (g/l) of				
		150	175	200	225	250
G-6	untreated	18	13	< 1	< 1	< 1
G-6	S	> 200	> 200	160	132	110
G-6	Q	> 200	173	47	35	27

Note) In all cases passivation times were measured at a C.D. of 400 A/m² and at 50°C after the anode samples had been preanodized for 24 h at 200 A/m² in conventional Cu electrolyte.

Table 2: Critical current densities measured for various copper anodes at 50°C

Anode	Passivation time at 400 A/m², min	Critical C.D. (A/m²)		
		Untreated	Treatment S	% Increase
B	94	247	338	36.8
G 2	23	215	320	48.8
G 4	16	197	266	35.0
G 6	12	180	275	52.8
E	12	215	315	46.5
D	6	220	320	45.5
F	3	215	310	44.2
K	3	175	290	65.7
L	1	170	290	70.6

Table 3: Effect of heat treatment S upon dissolution characteristics of copper anode.

Anode composition (%) ; 99.37 Cu, 0.17 O, 0.015 Ni, 0.121 As, 0.008 Sb, 0.0014 Bi, 0.008 Pb, 0.036 Se, 0.013 Te, 0.005 Fe, 0.01 Sn, 0.008 S and 0.0516 Ag.

Anode	Slime fall, kg/t Cu	Slime composition, %						
		Cu	Ni	Ag	Pb	As	Sb	Bi
Untreated	4.4	24.07	0.03	9.9	3.52	6.16	10.06	3.05
S-treatment	3.3	18.76	1.60	13.5	5.05	9.21	15.42	3.96

Table 4: XRD analysis of various anode slimes: effect of heat treatment S

Anode	Grade of phase	As Cast Phase Identification:	Heat Treatment S			
L	Major	UI(*), Cu_2O	Cu_2-x Se, NiO, Ag°			
	Minor	Cu_2-x Se, CuAgSe, Cu°, NiOOH			CuAgSe,	Cu_2Se
D	Major	$PbSO_4$	$PbSO_4$, PbO_2			
	Minor	Ni°, Cu_2O	NiO,	Ag°,	Ni°	
F	Major	$PbSO_4$	$PbSO_4$, PbO_2			
	Minor	Ni°, Cu_2O	NiO,	Ag°,	Ni°	
K	Major	UI(*), Cu_2-x Se	Cu_2-x Se, NiO,	Cu_2O,	CuAgSe	
	Minor	NiO, CuAgSe		Ag°	Ni°	Cu_2Se
B	Major	Cu_2O	Cu_2-x Se		CuAgSe	
	Minor	Cu_2Se, Cu°	$PbSO_4$	Ag°		Cu_2Se
C	Major	UI(*)	Cu_2-x Se,		CuAgSe	
	Minor	Cu_2O, Cu°, 6 Cu_2O·CuO		Ag°		Cu_2Se
L' (**)	Major	Cu_2O, NiO	Cu_2-x Se, NiO	Ag°		
	Minor	Cu° UI(*), CuAgSe			CuAgSe	Cu_2Se

(*) UI denotes unidentified phase.

(**) Anode L was remelted, then air cooled.

Table 5: Analysis of the suspended slimes formed during electrorefining of two typical copper anodes with and without heat treatment (annealing + slow cooling)

A) Chemical composition (ppm)

	O	Ni	Pb	As	Sb	Se	Te	S	Bi	Sn	Ag
Anode A	2000	3750	54	15	<3	380	66	10	18	12	395
Anode C	1000	244	41	66	66	235	17	5	3	4	246

B) Amount of suspended slimes formed (mg/l)

Anode	Untreated	Slow cooled
Anode A	18	12
Anode C	11	4

C) Cathode quality (ppm)

Sample	Treatment	Au	Ag	Se	Te	Sb	Bi	As	S
Anode A	untreated	<5	9	0.7	<1	1	0.8	3.9	<5
"	slow cooled	<5	2	<0.1	<1	<0.1	<0.1	1	<5
Anode C	untreated	<5	4	0.9	<1	1.9	<0.5	2.5	<5
"	slow cooled	<5	1 .	<0.1	<1	<0.1	<0.5	<1	<5

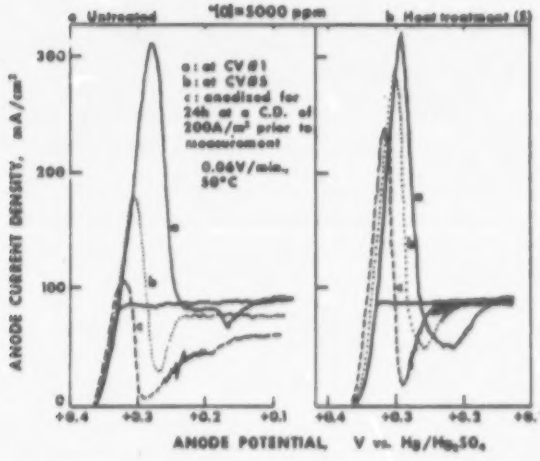

Figure 1: Cyclic voltammetric curves showing the beneficial effect of heat treatment S upon dissolution activity of high-oxygen anode.

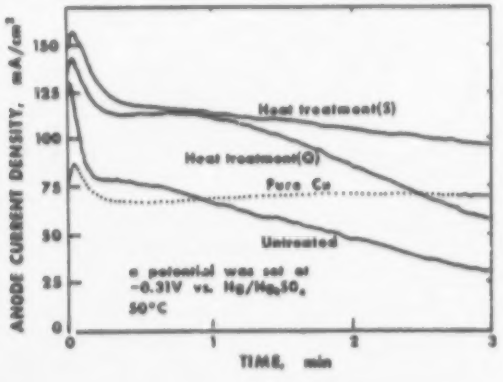

Figure 2: i-t decay curves showing the effect of heat treatments S and Q.

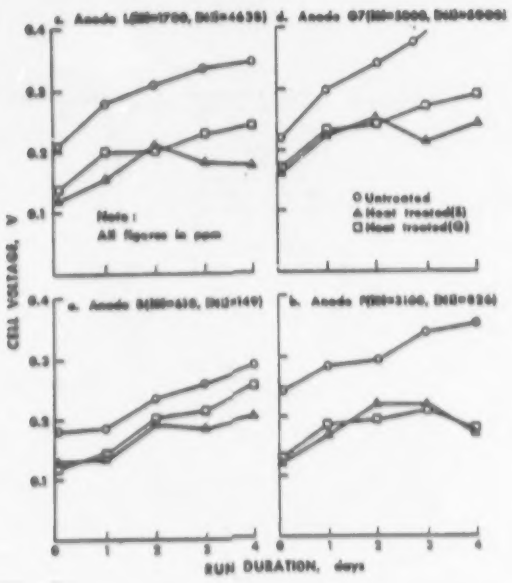

Figure 3: Cell voltage versus time curves of typical copper anodes at 200 A/m^2

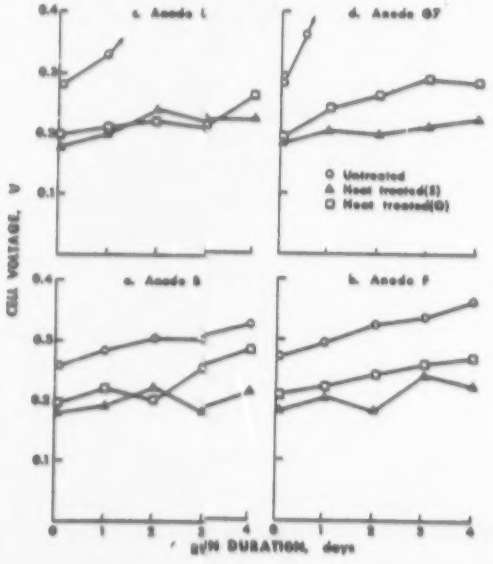

Figure 4: Cell voltage versus time curves of typical copper anodes at 300 A/m^2

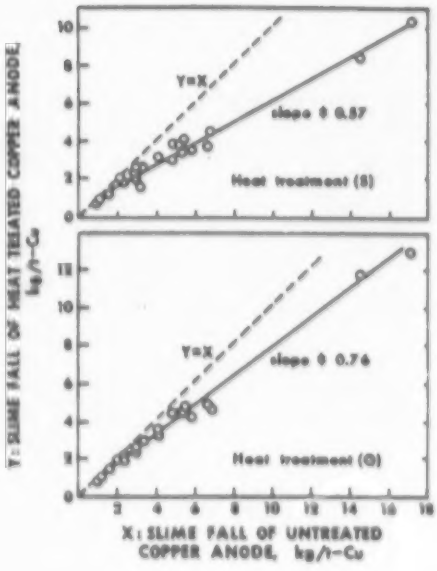

Figure 5: Effect of heat treatment upon slime fall of various copper anodes.

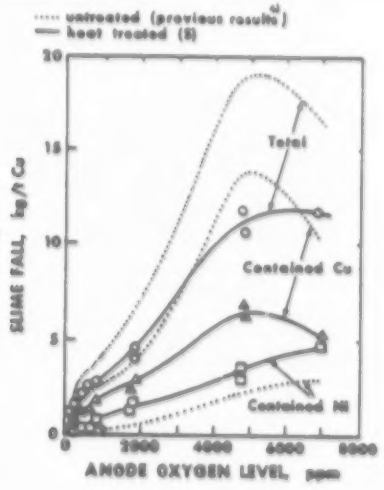

Figure 6: Slime fall versus anode oxygen level: effect of heat treatment S

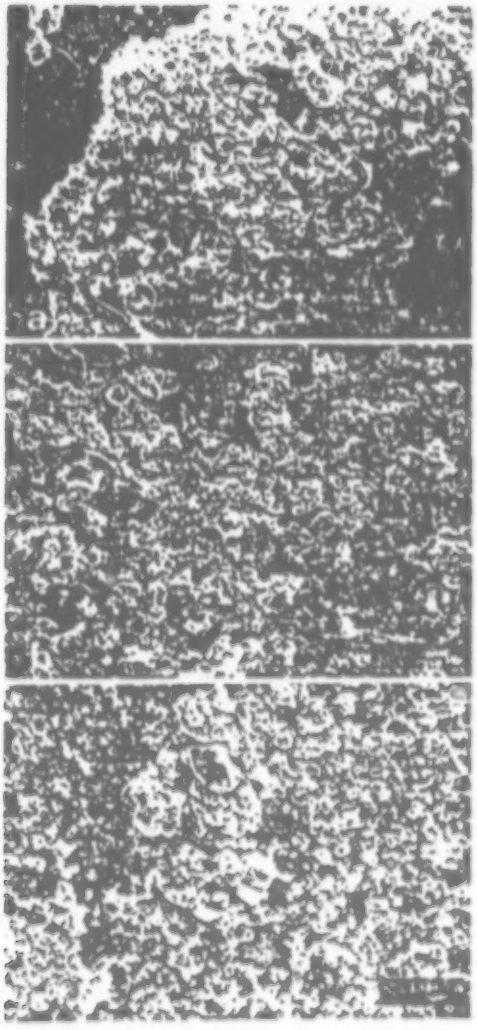

Figure 7: Micrographs showing the slime particles from (a) untreated, (b) S-treated and (c) Q-treated anode L, respectively.

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Effect of Anode Impurities upon Passivity of Copper Anodes*

— Anode passivation in copper refining (11th Report) —

by Shin-ichiro ABE[1] and Sakichi GOTO[2]

A susceptibility of copper anodes to passivate greatly increases when both oxygen and nickel levels are high therein. Slime analyses also indicate the possibility that anode nickel is responsible for the increased tendency of the slime layer to become more colloidal, thus impeding the Cu^{2+} ions from diffusing across this layer and hence promoting the onset of passivation.

A high-Ag anode (typically 2,600 ppm) also exhibited its great susceptibility to anode passivity due largely to the very dense and thick slime layer adhered to the surface.

A correlation was not clear between the anode lead content and tendency to passivate.

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1. Foreword

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In a previous general study of copper anode passivation,[1)] anode slimes which were obtained in an electrolytic experiment on 13 kinds of crude copper provided by 9 copper electrolytic refineries were collected and kept. The slimes will be studied here again. The point of this study is to see whether it is possible to find some relationship between the distributions of the slime compounds and anode passivation.

The effect of anode slime layers on passivation is great. This has been proved from various points of view.[1)-5)] The kind and amount of

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compounds which compose the barrier layers are highly related with the kind and amount of impurities in the anode parent metal. In the case of anodes made by INCO, the levels of oxygen and nickel are traditionally, and still, very high. Crude copper with a high nickel level is found in copper from many other electrolytic refineries. Refiners seem to think that because nickel has a baser electric potential than copper does, it will almost dissolve at the time of electrolysis, and that therefore the amount of nickel, even if it is fairly high, does not do any harm. However, one of the conclusions obtained from a series of studies in the past is that "anode nickel is dangerous, and that especially when the oxygen level is high, the danger becomes double."[2)]

Through x-ray diffraction analyses of the above mentioned slime samples, it became clear that most of the compounds are mainly made of four major elements: Cu, Ni, Ag, and Pb.[a)]

Therefore, in this study, we decided to extend our discussion to Ag and Pb as well as to oxygen and nickel.

2. Results and Discussion

2.1 X-ray diffraction analyses of slimes

Table 1 shows a simplified version of the results of the detailed

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a) Contrary to our prediction, compounds like As, Sb, Bi were not detected. This is because the copper electrolytic solution used here was synthetic and relatively fresh, therefore, metal ions in the solution did not reach the equilibrium concentration, resulting in no precipitate of compounds.

phase identification of all the slime samples. It shows only major and minor phases for simplicity, but the analyzed values of O, Ni, Ag, and Pb, extracted from Reference 1) are added here. In this table, the crude coppers are arranged in such a way that the tendency of passivation increases ($t_p \longrightarrow$ sa...l)[b] in downward order.

The harmfulness of oxygen has been discussed in many places.[1)2)] The point is that the increase of the oxygen level causes an increase of Cu_2O compound, which enters the slime layer. However, as is obvious from Table 1, it is not easy to find a relationship between passivation and the oxygen level alone, ignoring the distribution of other anode impurities. For instance, the oxygen level of the crude coppers K and L is about 1,700 ppm each and it is considerably lower than that of the crude copper F, which is 3,100 ppm, but the t_p of the former two is one minute and this is much shorter than the 11 minutes of the latter. This is because the distribution of other anode impurities 430
besides oxygen is fundamentally different between the two groups. Especially the nickel levels are remarkably different.

Similar examples are found in the passivation behaviors among the crude coppers D, E, F. Although these crude copper samples were made in the same copper electrolytic refinery at almost the same period,[c)]

b) The time consumed from the start of electrolysis, loading a certain level of electric current density (400 A/m^2), to the sudden rise of anode electric potential is defined as t_p. The measurement was performed using standard copper electrolysis (40g/L Cu, 200g/L H_2SO_4, 20g/L Ni, solution temperature 50°C) with anodes, on which slime layers with quasi-equilibrium thickness have been formed beforehand by electrolysis at 200 A/m^2 for 24 hours.

c) However, the reason why the levels of oxygen and nickel are quite different is unknown.

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it is reported that only anode D dissolved smoothly in the tank house, while E and F showed repeated periodic passivations. In fact, confirming this report, t_p values for the three samples in our experiment decreased in the order D→E→F. In the previous report,[1] we could not find the reason for this, but it is now possible to consider that this is related to the oxygen and nickel levels. That is, among these three crude copper samples, in which the distributions of impurities except Pb are almost the same within certain limits, the level of oxygen increases in the order D→E→F. In this case, a very stable refractory NiO was generated inside the anode texture when it was cast, and it seems that the more the level of oxygen increased, the more this oxide formation reaction was promoted. In fact, the amounts of slimes formed by electrolysis of the anodes D, E, F, increased in this order to a quite large extent: 2.1, 3.2, and 3.8 kg/t Cu. The chemical analyses of the slimes revealed that the increase of the amounts of copper and nickel compounds is the main cause for this. (See Table 2).

On the other hand, the lead content in the crude coppers D, E, F increases in this order, but it seems unreasonable to relate this directly with the tendency of passivation, because the tendency of passivation of various crude coppers, in which $PbSO_4$ compound is the major phase of the slimes, has a large variation and is not consistent. Of course, if we suppose a case in which the basic compositions are fixed and the level of lead only is increased gradually, there is no doubt that the tendency of passivation increases because the $PbSO_4$ generated and deposited in the anode slimes of the crude copper increases accordingly.

Letskhiki et al[6] report that when the lead content was fixed at 0.24, 0.08, and 0.05%, the time for passivation increased accordingly in this order: 4, 5.5, 7.5–8 hours at 400 A/m^2. Also, Ito et al[7] report that although no substantial change was detected on the polarization curve of copper anodes when the lead content was adjusted in the range of 0.39–1.50%, the t_p values decreased in accordance with the increase of the lead content.

According to a report on an electrolytic pilot test done in an Australian copper electrolytic refinery,[8] when the level of anode lead was fixed at 0.5% experimentally, problems such as a rise of the cell voltage and a quite significant increase of formation of slimes* happened right after the start of electrolysis. Therefore, it is reported that in the actual refining operation, the lead content of anodes is controlled to maintain lead at less than 0.25%.

As long as the content is controlled below a certain level, even if $PbSO_4$ remains in the major phase, lead does not affect passivation severely because this compound is considered to consist primarily of particles that are completely crystallizable and dispersible. On the contrary in the slimes generated by the above-mentioned crude coppers K and L, which contain a large amount of nickel, another nickel compound (γ-NiOOH) distinct from the NiO compound, although in very small amount, was detected. This substance is very colloidal, and hydrometallurgical engineers have often experienced bad filtration of this cake. Even if the amount is very small, if the whole anode slime becomes colloidal because of it, the ability of copper ions to diffuse in the barrier layers will be largely restricted. As mentioned before,[2] according

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* translator's note : literally "maternity room"

to observations by a scanning electron microscope on the two groups of the slime layers generated on the surfaces of the anodes G and L, the slime of the crude copper L, which contains twice as much nickel as G, are far thicker and denser than the slime of G, which has $PbSO_4$ as a major phase. Therefore, passivation occurred more easily on the crude copper L. This is a good example to prove the above argument.

In summary, we can conclude that "anode oxygen is harmful, but that if the nickel content becomes high at the same time, the harmfulness will increase all the more." If we discuss the effect of oxygen without paying attention to anode nickel (or vice versa), we cannot fully understand the passivity phenomena. As one example, after a group of crude copper samples in which levels of oxygen are adjusted to various extents, was electrolyzed,[2] we plotted the ratio of copper and nickel compounds which entered the anode slimes as a function of anode oxygen level. (Fig. 1). It is obvious that the ratio increases in a straight line when the oxygen level is under 850 ppm. This is 431
because the anode nickel is still metallic below this level and exists inside the tissue. Therefore, at the time of refining, most of it dissolves and only a little enters the slime. However, when the oxygen level goes above 850 ppm and increases gradually, part of the surplus oxygen starts to separate out in a mosaic state along the grain boundary and combines with nickel to form stable NiO. Then the graph declines in a straight line.

2.2 Passivation behavior of high-silver anodes

Let us now take a look at the effect of silver on copper anode passivation. If the theory that "under any circumstance, any cause that makes anode slime layers thick and dense tends to cause passivation", is applied, we have to pay attention even to silver, which is not usually discussed, if it is present in anodes.

From Table 1, it is obvious that the silver compounds which are usually detected in slimes are mainly Ag^0 and/or CuAgSe. According to Greiver's study,[9] if silver or selenium becomes excessive in anodes, the CuAgSe phase will not be detected in slimes anymore, and Ag^0 and/or $Cu_{2-x}Se$ are generated instead. If we compare the crude coppers I and J in Table 1, where the silver level in the latter is 4 times as high as in the former, we can clearly detect the process of phase transformation of the slime composition from CuAgSe to Ag^0 according to the increase of silver. The crude copper J which has a higher silver content was passivated more easily.

In 1980, a severe passivation problem happened in the INCO copper electrolytic refinery in Sudbury. The production efficiency level of copper dropped down to 89% at one time. The results of our experiment in search for the cause are as follows. The time when this problem happened coincides with the time when the Doré furnace was being repaired. At that time, bricks for furnace construction, on which silver solid matter was attached thickly, were thrown in the refinery furnace directly, and then an anode with a high-level (2,600 ppm) of silver was distributed throughout about half of the tank house. This serious operational error continued for about 10 days until the level of the anode silver went back to be normal. We can judge from

this that the cause of the anode passivation was the high level of silver.

Two kinds of anodes were given to us by the Sudbury electrolytic refinery. One is a regular anode and the dissolution surface is smooth, but the other high-Ag anode which was coil-shaped has a rough, uneven, and shiny dissolution surface. It seems that the latter has been already passivated in the tank house. From the chemical compositions of the two anodes (Table 3), we can tell that the regular anode is a good one whose impurity level is well controlled. However, the Ni level is very high. The high-Ag anode has almost the same impurity distribution as the regular one, but the silver content is unusually high - about 5 times as high as normal. The palladium level is also 5 times as high as normal, but the amount is only 70 ppm and negligible compared to the amount of silver, therefore it is omitted from this study.

Two kinds of crude copper samples cut in the size 14cm x 12cm x 0.7 cm were electrolyzed for 5-6 days in an electrolytic cell with a capacity of 18 L, filled with the standard copper electrolysis solution at 60°C. Fig. 2 shows changes of the cell voltage at current density 200 A/m^2 with the passage of time. It is confirmed that the high-Ag anode was gradually passivated after 5 days, as observed in the actual refinery. However, the regular anode did not show any trace of passivation even after 5 days. 432

After each dissolution test, pictures of generated anode slimes (wet) were taken. (Fig. 3). As it is clear from the pictures, the slime layer formed on the surface of the high-Ag anode was very thick and dense. The attachment to the surface was so strong that even a small piece of slime did not come off during the whole 6 days of electrolysis. The t_p value of this anode was one minute, while the t_p of the

regular anode was 9 minutes, showing a high activity of dissolution.

The amount of slimes generated from the high-Ag anode was 7.2 kg/t Cu, which was more than double that of the regular one (2.8 kg/t Cu). The slimes of the both anodes were examined by chemical and x-ray diffraction analyses after they were washed with water and dried. From the results of the chemical analysis shown in Table 4, we know that the reason why the amount of slimes formed by the high-Ag anode became unusually high is the increase of the amount of silver and copper compounds. The increase of Ni, Se, and Te was detectable, but it was much lower than that of silver and copper. The silver level in the slimes increased 5 times. This matches with the ratio of the silver levels of the regular and the high-Ag anodes. Obviously it is because almost all of the anode silver entered the slimes.

According to the results of the phase identification in Table 5, both slimes contain Ag^{o} and Cu_2O as major phases, and NiO, $PbSO_4$, and the unidentified phase (UI) as minor phases. Only slight amounts of Cu^{o} was detected. It was observed that another major phase in the slimes from the regular anode, CuAgSe compound, disappeared completely when the silver level increased 5 times. This was already discussed in 2.1.

Regarding the disbribution of the slime compositions stated above, there is another thing which should not be overlooked. That is, when a possible relationship between the distributions of anode impurities and the generated slime structural compounds is being studied, it is important to know how and under what circumstances the anode in question was cast. To support this, two experimental examples will be given.

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1) One crude copper, and another which was dissolved and re-solidified in a laboratory scale were electrolyzed under the same conditions. A difference was found between the distributions of the slime compounds generated from these crude coppers. The cause could be the different cooling speeds in the two.[10)]

2) The crude coppers C and H, which were provided by different copper refineries, have quite similar compositions. (Table 1). However, the distributions of the compositions of the generated slime compounds C and H are quite different. Since the slimes were generated under the same electrolytic condition, the difference, even if it is slight, seems to be due to different treatments such as different cooling speed, etc. during copper casting in the two refineries.

3. Conclusions

From the discussion in this study, the following conclusions are drawn.

(1) When the effect of oxygen on the passivation of copper anodes is discussed, one should pay attention to the level of anode nickel at the same time. The susceptibility to passivity increases greatly when both oxygen and nickel levels are high in the crude copper.

(2) It is quite possible that some nickel compounds in slimes are colloidal. In this case, they impede the copper ions from diffusing across the slime layer.

(3) The effect of $PbSO_4$ compound deposited in the slime layer upon anode passivation is not so strong as that of nickel.

(4) The slime layer formed on the surface of a high-Ag anode (Ag=2,600 ppm) is very thick and dense. Also its attachment is very strong. Consequently, passivation occurs easily.

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Table 1 Phase identification of various anode slimes.

Anode	Impurity level (ppm) O	Ni	Pb	Ag	Phase identified (*)		Passivation time t_p (min)
B	610	149	45	288	Cu_2O	Cu_2Se, Cu^o	98
C	1000	244	41	246	UI	Cu_2O, Cu^o, 6 Cu_2O·CuO	14
D	1500	932	1174	227	$PbSO_4$	Cu_2O, Ni^o	17
E	2300	1473	1320	197	$PbSO_4$	Cu_2O, Ni^o, NiO	12
F	3100	826	1982	222	$PbSO_4$	Cu_2O, Ni^o, NiO	11
G	1800	2237	571	337	$PbSO_4$	Cu_2O, Ag^o, $Cu_{2-x}Se$, CuAgSe	10
H	1100	226	53	233	Cu_2O, $Cu_{2-x}Se$	Ag^o, CuAgSe, $PbSO_4$	6
I	1300	290	1360	1500	$PbSO_4$	CuAgSe	6
J	1400	1788	633	5500	$PbSO_4$, Ag^o	UI, NiO	4
K	1600	4565	50	350	UI, $Cu_{2-x}Se$	NiO, CuAgSe	3
L	1700	4638	83	352	NiO, Cu_2O	Cu^o, CuAgSe	1
M	3900	569	919	950	$PbSO_4$, Ag^o	Cu_2O	1

(*) UI denotes unidentified phase.

Table 2 Chemical analyses of anode slimes D, E and F.

Anode slime	Composition, % Cu	Ni	Pb	Ag	Slime fall, kg/t Cu
D	19.8	2.23	5.1	1.12	2.1
E	23.4	3.19	4.2	0.63	3.2
F	27.5	4.92	5.0	0.56	3.8

Table 3 Compositions of copper anodes from two different sources.

	Impurity level, ppm O	Ni	Pb	As	Sb	Fe	Bi
Regular anode	900	4200	80	79	14	6	25
High-Ag	1100	4700	130	36	8	11	15

	Impurity level, ppm Sn	Se	Te	Au	Ag	Pd
Regular anode	30	340	80	5-20	460	12
High-Ag	47	460	500	10-50	2600	69

Table 4 Chemical analysis of anode slimes formed from regular and high-Ag copper anodes.

Sample	Slime Composition, wt % Cu	O	Ni	Pb	Sb	Fe	Bi	Sn	Se	Te	Au	Ag	Pd
Regular anode	24.9	14.7	4.23	0.53	0.13	1.51	0.16	0.76	11.80	2.84	0.41	17.8	2.18
High-Ag anode	28.5	6.1	4.33	0.47	0.07	0.15	0.12	0.48	9.56	7.19	0.51	35.2	1.58

Sample	Element Disposed, kg/t Cu Cu	O	Ni	Pb	Sb	Fe	Bi	Sn	Se	Te	Au	Ag	Pd
Regular anode	0.71	0.42	0.12	0.015	0.004	0.043	0.005	0.022	0.335	0.081	0.012	0.51	0.062
High-Ag anode	2.05	0.44	0.31	0.034	0.005	0.011	0.009	0.035	0.687	0.517	0.037	2.53	0.114

Table 5 X-ray diffraction phase identification.

Slime obtained from	Major Phase	Minor Phase	Very Minor Phase
Regular anode	Cu_2O, Ag^o, CuAgSe	UI(*), NiO, $PbSO_4$	Cu^o
High-Ag anode	Cu_2O, Ag^o	UI, NiO, $PbSO_4$	Cu^o

(*) Unidentified phase

Note that some palladium compound was also detected in both samples, and its phase is tentatively $(CuPd)_2Se_4$.

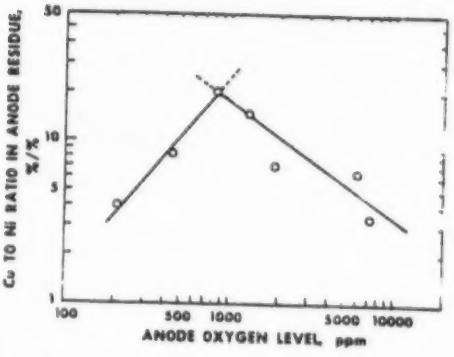

Fig. 1 Ratio of Cu to Ni entering the anode residue plotted as a function of anode oxygen level.

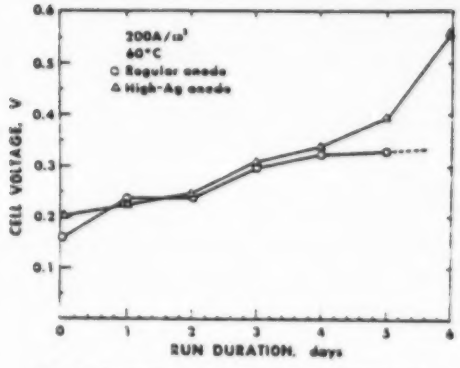

Fig. 2 Cell voltage versus time curves obtained with regular and high-oxyge copper anodes.

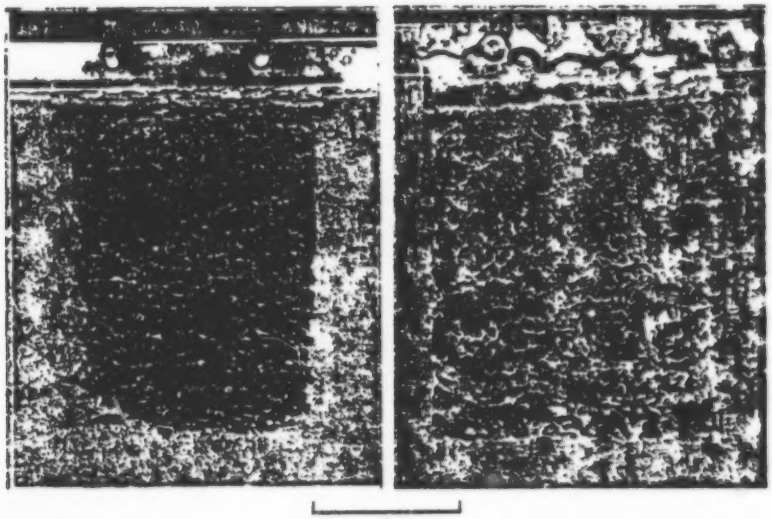

Fig. 3 Corroded surfaces of both regular and high-Ag anodes.

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Some Consideration on the Structure of an Anode Slime Layer*

- Anode passivation in copper refining (12th Report) -

by Shin-ichiro ABE[1]

Summary

An attempt was made to find a way of expressing in a numerical fashion the average pore size that an anode slime layer has. The method involves first obtaining basic relationship between passivation time, critical current density and pore size by using so called 'simulated aged anode' as prepared by firmly holding an artificial slime layer (i.e., Millipore filter papers with different pore sizes 0.22 - 8.0 μ) against the surface of a pure copper anode, and then correlating these data to those obtained for 'real' slime layers.

The pore size of a 'real' slime layer is numerically expressed by the following equation,

$$\log W = a - b \log (P.S.)$$

where W is the amount of slime formed, kg/t-Cu, and P.S. is the pore size, μ. The pore size so obtained does not have any academic significante; yet it seems useful enough to give a relative indication as to whether one particular slime layer in question is denser or more porous compared to the other, or whether the original pore size turns denser or looser when the electrolytic conditions are changed.

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* Received Dec. 6, 1982.

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1. Foreword

The role played by the anode slime layer in the passivation of crude copper anodes during refining in an electrolytic bath is extremely great. This is why one must remove rapidly the eluted copper ions from the surface of the poles in order to perform smooth electrolytic refining while preventing the deposit of a copper sulfate salt film on the anode surface. In this case, the driving force of the substance transfer is diffusion and viscous flow by gravity[1]. Regardless of the pattern, these motions can proceed only through the pores of the anode slime layer. Consequently, it is not exaggerated to say that the 2 essential parameters (layer thickness and porosity) controlling the structure of this slime layer (which must be called a 3rd system caught between the 2 systems which are the anode and the electrolyte) hold the key to copper anode passivation.

In the past series of studies, we explained rationally the observed phenomenon of passivation while touching frequently upon the slime layer porosity. In fact, however, the porosity has not been

measured, and there are only two instances of scanning electron microscopes being used to observe the shape of the slime layer during actual operations.[2) 3)]

The thickness of the anode slime layer is a measurable number. In contrast, determining the porosity is so difficult that it is next to impossible. This is not only because of the complexity of the slime layer structure itself but also because the continuous growth during electrolysis accompanied by unceasing changes of shape and by local break-ups. In short, it is not exaggerated to say that the slime layer cannot have an absolute structure. Therefore, the fact is rather that under given electrolytic conditions the porosity of the slime layer forming to cover the polar surface of a given crude copper anode is essentially known through the so-called "average" shape exhibited during the entire growth process. Another important consideration is that one should not endeavour to seek the absolute value of the obtained "average" porosity but rather think of porosity as high or low according to a relative index through comparisons based on various crude coppers. It is also more practical to be able to use the relative index to know the variations brought about when changing variously the electrolytic conditions.

In the present study we examined the method of describing porosity relatively in terms of "average" shape, using numerical values with regard to various actual slime layers. The results are as follows.

2. Testing method

In Millipore filter paper (MP paper) which so far we often employed as artificial slime layer[4)5)], the size of the pores,

the porosity[a)] and thickness are rigorously standardized. It is a product extending uniformly in the thickness direction of the MP paper because there is no communication between the individual pores.

In the present study we investigated in terms of pore function the continuous passivation characteristics of so-called "simulated aged anodes" obtained by combining this MP paper and pure copper anodes. We applied the obtained results to actual slime and examined the possibility of describing numerically the "average" shapes of the porosity.

The pure copper anodes employed were built by cutting rectangular parallelepipeds of 2 cm x 2.5 cm x 1 cm out of electric copper, embedding them in epoxy resin (the final shape was circular, the diameter of the base plate being the same as that of the MP paper). The exposed parts were given a mirror-like finish and we pressed firmly against these parts of MP paper of various pore sizes ranging from 0.22 μ to 8 μ, without allowing any interstice. Therefore, we performed a series of electrolytic tests in standard copper electrolyte (40 g/L Cu, 20 g/L Ni, 200 g/L H_2SO_4). The temperature was set at 50°C.

The MP paper used as artificial slime layer was allowed to soak for one night in the above standard copper electrolyte before usage, was then transferred to a beaker and desiccator and by repeating absorption and normal pressure, the air entrapped within the pores was replaced by the solution.

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a) The proportion of area occupied by all pores vs. the total external area of the MP paper is usually around 80%.

3. Results of the tests

3.1 The artificial slime layer

Regardless of the pore diameter, the film thickness was roughly constant at 120 μ with the series of MP papers employed. Fig. 1 shows the results obtained by plotting the passivation times (t_p) found by loading a constant current density of 400 A/m^2 on the simulated aged anode against the logarithms of the pore size (pore size; P.S.). p. 520

As the graph shows, a gradual t_p increase can be expected as the diameter of the pore grows larger. After a regular progress, the increase speed begins to gradually slow down as the diameter of the pore reaches 1.2 μ. When the 10 μ range is reached, the curve levels off. This is similar to the previously reported[6] phenomenon always accompanying the formation of fine copper powder at the time of pure copper anode dissolution. The particle diameter of this copper powder ranges from about 1 to 20 μ, and part of this powder seems to clog the pores of the MP paper during electrolysis.

Following this, we sought by the 200 ~ 1,000 A/m^2 current density and with regard to the respective pores the passivation times of the anode employed above. Fig. 2 shows the results obtained reexpressed in $t_p^{-\frac{1}{2}}$ vs. C.D. terms. As the Graph for the pore diameters 0.45 μ and 0.8 μ is quite simple, it is omitted here. In all cases, a good rectilinearity is obtained. The points where these extended straight lines cross the axes are the so-called critical current densities (i crit.)[2] and are the particular values with regard to the "aged anodes" of the given porosity.

Fig. 2 shows also the measurement values obtained when using polyethylene sheets (actually there are no pores). Since at the very

time the current was sent, the anodic electric potential rose suddenly (in fact $t_p = 0$), we ascertained that polyethylene film was firmly attached so as to prevent crevices on the anodic surface and so as to avoid leak current formation.

Fig. 3 shows the replotted i crit. vs. P.S. correlation derived from Fig. 2. It should be obvious that there is a rectilinear increase in i crit. value with regard to log (P.S.). Here also, as seen in the already explained Fig. 1, we observe a loss of rectilinearity above the pore diameter of 1.2 μ.

If we assume that the aforementioned rectilinearity shown in Fig. 3 will be sustained even above a 1.2 μ pore diameter if there is no obstructing effect from the generated copper powder, then the following relationship would be produced between i crit. (A/m^2) and the pore diameter (μ):

$$\text{i crit.} = 180 + 175 \log (\text{P.S.}) \qquad (1)$$

3.2 The actual slime layer

We electrolyzed various types of actual copper[b] for 2-4 days with a current density of 200 A/m^2, and weighted the generated anodic slime. Meanwhile we gave a previous 24 h anodic treatment to the same series of crude copper sample pieces as above, and after allowing the formation of a quasi-equilibrated thickness slime layer[c], sought the i crit. values for these "aged anodes". Fig. 4 (Graph a) p. 521

b) The electrolytic samples used in reference (2) were obtained from 9 companies.

c) The discussion is pursued while assuming that the thickness is about the same (110-140 μ) as that of artificial slime layers, that there is practical identity with simulated aged anodes and that there will be no serious subsequent deviations.

shows the correlativity of the volumes of slime formation so obtained vs. the i crit. We also show (Graph b) the similar results obtained with regard to samples activated at high temperature (annealing + slow cooling) reported earlier[7].

These results show evidently that:

(1) regardless of the type of crude copper the i crit. values rise as the volume of slime formation drops. In short, passivation is unlikely to occur.

(2) even when the volume of slime formation is the same, the porosity of the slime layer on the heat-treated crude copper is considerably higher than with untreated copper.

From the above Fig. 4, the following correlation formulae are respectively derived between the volume of slime formation (W: kg/t Cu) and i crit. (A/m^2):

$$\text{(untreated)} \quad \log W = 2.417 - 0.0094\ i_{crit.} \qquad (2)$$

$$\text{(heat-treated)} \quad \log W = 3.339 - 0.0095\ i_{crit.} \qquad (3)$$

If combining respectively formulae (1) and (2) as well as (1) and (3), we try to establish the relationship between the volume of anode slime formation and the "average" porosity of this slime, we obtain:

$$\text{(untreated)} \quad \log W = 0.725 - 1.645 \log (P.S.) \qquad (4)$$

$$\text{(heat-treated)} \quad \log W = 1.630 - 1.663 \log (P.S.) \qquad (5)$$

Fig. 5 is obtained by plotting these formulae. The data of Graph (a), (b) in Fig. 4 give the i crit. values contained in the 100-250 A/cm^2 range regarding the former and similarly within the 250-350 A/m^2 values regarding the latter so that the respective pore diameters corresponding to these current density ranges are shown by solid lines in Fig. 5.

The view regarding the "average" porosity[d] of the slime layer deducted from the Fig. is as follows. When electrolyzing high-oxygen copper G-6 very likely to undergo passivation, one obtains the 17 kg/t Cu slime formation value. The average porosity of this slime is 0.46 µ. Meanwhile, the volume of slime formation on the G-0 anode which is completely similar in impurities distribution to the G-6 and other anodes but is only rather low in oxygen contents, is 5.8 kg/t Cu and about 1/3 that of G-6 so that the average porosity increased about twofold (0.9 µ). When both t_p values were measured, G-0 showed 12 min and G-6 showed 6 min.

As reported already,[8)9)] when crude copper is heat-treated (slow cooling) the dissolution behaviour differs greatly and variously from that of untreated copper. The amount of slime formation drops. For instance, with the former G-0 anode it is 3.5 kg/t Cu, and with G-6, it is 9.5 kg/t Cu which represents a significant drop. If we look at these values in the Graph of Fig. 5, we see that the "average" porosities at the moment when the anode slime layer reaches clearly the equilibrated thickness are respectively 4,4 µ, 2.4 µ when expressed numerically. Whichever we consider, we can see that with heat treatment, the porosity of the slime layer is considerably higher than with untreated copper. For both, the measured t_p values are above 200 min and the dissolution activity rose to a level such that under normal electrolysis conditions passivation became completely impossible.

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d) Pore size assuming the formation of the same film as the 120 µ thick, 80% porous artificial slime.

One may accept the view that these phenomena take place because as all various dissolution activities rise through heat treatment, not only does the volume of slime decrease (that is, the thickness of the slime layer decreases and the diffusion flow of the Cu^{2+} ion is rendered smoother) and the activity of the anode itself increases[8], but also the porosity increases simultaneously leapwise[9].

4. Discussion

A considerably high current density has to be applied to induce the passivation of pure copper anodes. However, when the electrode surface is covered with filter paper made to act as artificial slime layer, passivation is easily induced with a very low current density of 200 A/m^2, let alone 100 A/m^2. From this example one may evaluate how important the anode slime layer thickness is.

The effectivity of refining anodes is great. It contributed largely in Japan first to raise the quality of electrolytic copper and to the rationalization of electrolysis in most copper in refineries. However as usual, whenever anodic impurities are contained, the formation of anodic slime is inevitable. Consequently efforts to decrease the generation of the slime layer forming on the surface of copper anodes, and to control slime types which do not inhibit too strongly the diffusion of Cu^{2+} ions through their physical properties (thickness and porosity) are essential with regard to managing passivation prevention. Throughout the entire 3 fields constituting the electrolytic refining system, viz., the copper electrolyte, the crude copper anode and the anodic slime layer, one must find one by one the factors leading to denser slime layers. Discovering measures toward a solution is the object of the series of studies conducted so far[1)-12)]. p. 522

This study was an attempt at describing the porosity numerically. The figures obtained have no scholarly value whatsoever. Compared to the MP whose geometrical structure is strictly determined, the structure of slime in actual operations is most complex so that it would seem meaningless to link both and to derive some relative correlation.

However the graph in Fig. 5 was conceived from the notion that by knowing the volume of slime generated it would be possible to know the porosity through the "average" shape and this might be used with any kind of crude copper anode. Unlike in the former attempts in which it was only possible to determine qualitatively whether the slime was dense or porous, we described numerically the porosity of the slime layer which was the real question, and so we may have provided some additional help toward grasping the shape of the slime layer.

5. Conclusion

We attached firmly a series of MP papers whose pore diameter ranged widely from 0.22 μ to 8 μ to the surface of pure copper anodes, and using "simulated aged anodes" examined their dissolution characteristics. We used the results on actual slimes, attempted to express quantitatively the porosity and derived the following correlative formula:

$$\log W = a - b \log (P.S.)$$

(W: amount of slime generated, P.S.: size of slime porosity)

The slime porosity computed through this formula does not have too much theoretical meaning but should be seen as quantification providing a relative index of porosity or density when comparing to one another other various crude copper slime layers. Moreover, by changing variously the electrolytic conditions or by thermal treatment of the

crude copper itself, the physical characteristics of the generated slime layer will as expected differ according to the times even when using the same crude copper. In order to know in such cases to what extent the slime layer will swell or shrink, the method of quantitative porosity expression used in this study should be sufficiently practical.

The main conclusions drawn from this study are as follows:

(1) Regardless of the type of crude copper, the critical current density of crude copper with small slime generation increases. In other words, passivation does not take place easily. The reason is not only that the slime layer is thin but also that the porosity increases simultaneously.

(2) Regarding the adverse effect of anodic oxygen upon anodic passivation, the reason seems to be that the porosity of the slime layer drops as the volume of oxygen increases.

(3) The reason why, regardless of crude copper type, high-temperature treatment activates strongly the dissolutions is not only that the generation of slime drops but also that porosity increases greatly at the same time.

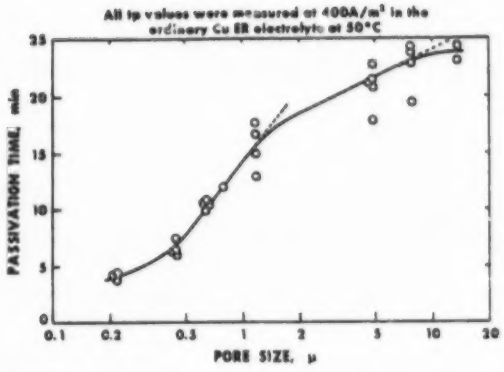

Fig. 1 An artificial slime layer study: passivation time of pure copper anode with Millipore filter paper of different pore sizes held against its surface.

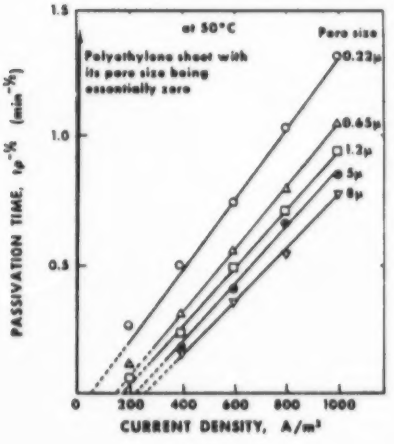

Fig. 2
Passivation time versus current density obtained at differing pore size of an artificial slime layer (Millipore filter paper).

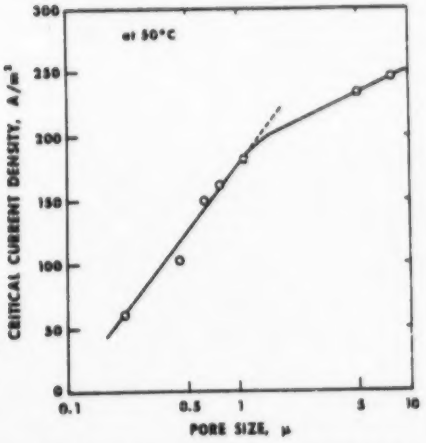

Fig. 3 Critical current density versus pore size of an artificial slime layer (Millipore filter paper) held against the surface of a pure copper anode.

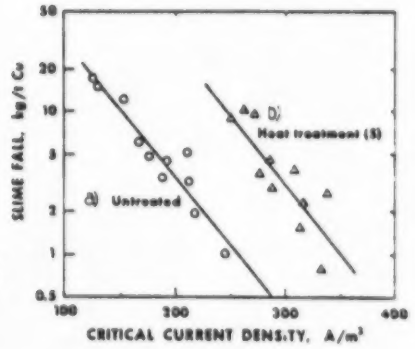

Fig. 4
Slime fall versus critical current density.

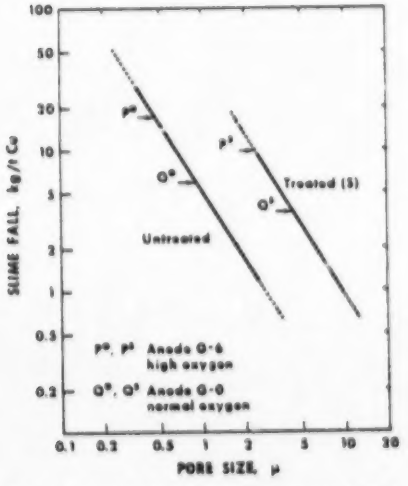

Fig. 5 A relationship between slime fall and physical resistance of the slime layer represented by pore size.
Note: The relationships were calculated based on the data shown in Figures 3 and 4.

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Summary

An attempt was made to find a way of expressing in a numerical fashion the average pore size that an anode slime layer has. The method involves first obtaining basic relationship between passivation time, critical current density and pore size by using so called 'simulated aged anode' as prepared by firmly holding an artificial slime layer (i.e. Millipore filter papers with different pore sizes 0.22 – 8.0 μ) against the surface of a pure copper anode, and then correlating these data to those obtained for 'real' slime layers.

The pore size of a 'real' slime layer is numerically expressed by the following equation,

$$\log W = a - b \log (P.S.)$$

, where W is the amount of slime formed, kg/t-Cu, and P.S. is the pore size, μ. The pore size so obtained does not have any academic significance; yet it seems useful enough to give a relative indication as to whether one particular slime layer in question is denser or more porous compared to the other, or whether the original pore size turns denser or looser when the electrolytic conditions are changed.

POOR

QUALITY

ORIGINAL